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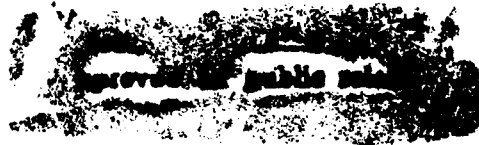


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ENGINEER RESEARCH AND DEVELOPMENT LABORATORIES

Report 1177

INTERIM REPORT

VAPORIZING FIRE EXTINGUISHING AGENTS

Project 8-76-04-003

18 August 1950

Submitted to

THE CHIEF OF ENGINEERS, U. S. Army

by

The Commanding Officer
Engineer Research and Development Laboratories

Prepared by

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SUMMARY

Subject. This interim report covers laboratory tests and research to develop a superior fire extinguishing agent, of low toxicity, suitable for use by troops in hand-portable containers under all climatic conditions. Work at the Purdue Research Foundation and at the Engineer Research and Development Laboratories during the period 1 January 1947 through 1 April 1950 is reported herein.

Investigation. Laboratory and practical fire tests were conducted, and corollary determinations were made of toxicity, corrosive action, electrical conductivity, as well as of the effects of temperature and of using different fuels and mixtures of different agents in inhibiting flame propagation. In both the laboratory and practical fire tests two agents, bromotrifluoromethane and dibromodifluoromethane, were found to be twice as effective as carbon tetrachloride, and in practical fire tests at -60 F bromotrifluoromethane was found to be most effective. This agent was also found to be of negligible corrosiveness, and the least toxic, in its natural chemical form, of the various fire extinguishing agents tested, including carbon dioxide. These data were correlated with the results of independent investigations. Where possible, the relationship between fire extinguishing effectiveness and the physical and chemical characteristics of the agents was explored.

Conclusions. It is concluded that:

- a. Of all the agents tested, bromotrifluoromethane best suits the actual military requirements for a fire extinguishing agent, and is superior to methyl bromide and carbon tetrachloride.
- b. As a military fire fighting agent, dibromodifluoromethane is equivalent to bromotrifluoromethane in all respects except that of toxicity.

Recommendations. It is recommended that service tests be conducted on bromotrifluoromethane as a fire extinguishing agent for Class B and C fires.

VAPORIZING FIRE EXTINGUISHING AGENTS

I. INTRODUCTION

1. Subject. This interim report covers laboratory tests and research to develop a superior fire extinguishing agent, of low toxicity, suitable for use by troops in hand-portable containers under all climatic conditions. Work at the Purdue Research Foundation and at the Engineer Research and Development Laboratories during the period 1 January 1947 through 1 April 1949 is reported herein.

2. Authority. This investigation was conducted under the authority of Project 8-76-04-003, Fire Extinguishing Agent, Improved, Self-Contained. The project card (RDB Form 1A) is contained in Appendix A.

3. Personnel and Cooperating Agencies. The work was carried on by the following project engineers, under the supervision of K. L. Treiber, Chief, Petroleum Distribution Branch, and T. B. Edwards, Acting Chief, Fire Apparatus Section: Eugene Elliot, 3 March 1947 to 20 March 1948; Kenneth C. Peck, 20 March 1948 to 31 September 1949; James E. Malcolm, 25 January 1949 to date.

The tests were accomplished by the following personnel of the Fire Test Area; James M. Hayden, Area Supervisor; Albert N. Williams, Group Leader; Edgar Helms, and Carrol Mahon, Fire Test Fighters.

Consultation on chemical phases of the project and laboratory fire tests were provided by the following personnel of the ERDL Materials Branch under the supervision of Arthur H. Van Heuckeroth, Branch Chief; Charles E. Green, Chief, Chemical Projects Section; Newell F. Blackburn, Chemical Projects Engineer; and Charlotte Boyle, Materials Engineer.

Purdue Research Foundation personnel working on the project under contract included: Dr. Earl T. McBee, Head, Chemistry Department; Dr. Zara D. Welch, Research Supervisor; and Dr's T. R. Santelli, C. E. Wheelock, A. Truchan, O. R. Pierce, R. A. Sandford, and D. D. Miccucci, research fellows.

Cooperating agencies include the Equipment Laboratory, Wright-Patterson Air Force Base, which has contributed funds to this project and has participated in the technical development; and the Civil Aeronautics Authority Experimental Station, Indianapolis, Indiana, which has supplied test data for inclusion in this report. The Medical Division of the Army Chemical Center conducted the toxicological screening investigation.

Private enterprises that have undertaken independent investigations and/or have made data available to the ERDL include: E. I. duPont de Nemours, Wilmington, Delaware; Minnesota Mining and Manufacturing Company, St. Paul, Minnesota; Pennsylvania Salt Manufacturing Company, Philadelphia, Pennsylvania; and General Chemical Division, Allied Chemical and Dye Corporation, New York City; Dow Chemical Company, Midland, Michigan.

Liaison has been maintained with the Naval Research Laboratory and the National Advisory Committee on Aeronautics, Washington, D. C., both of which have interest in a more effective and less toxic fire extinguishing agent.

4. Terminology. A terminology including the Underwriters' Laboratory fire classification, terms derived in the laboratory studies, and chemical nomenclature, is presented below:

Class A Fires. Incidences where the primary combustible material is of a solid nature. In most instances the material is cellulosic, i.e., wood, cotton, excelsior.

Class B Fires. Incidences where the primary combustible material is a liquid (almost always a hydrocarbon); however, this class covers solvent and liquid fuel fires in general.

Class C Fires. Incidences where electrical equipment or lines are involved in the fire; consequently, an electrically non-conductive type of extinguishing agent must be used to avoid danger to personnel.

Flame Inhibition. The forbiddance, interdiction, or prevention of the development of a flame.

Flame Extinction. The quenching or destruction of a propagating flame.

Agent. A fire extinguishing compound.

Flammability Peak. The minimum agent concentration, in percentage by volume, which will inhibit flame propagation in all possible concentrations of fuel in a fuel-air-agent mixture.

Fuel Ordinate. The fuel concentration, in percentage by volume, corresponding to the flammability peak.

Halocarbon. A compound containing atoms of carbon and one or more of the chemical elements fluorine, chlorine, bromine, and iodine. Usually, there are several ways of identifying any one organic (carbon) compound. Here, the most common or convenient

chemical name is used for the individual chemical compound, rather than an arbitrarily selected system that might produce for familiar compounds names unfamiliar to those not working in the field of organic chemistry. For the halocarbons, a nomenclature has been devised that satisfactorily identifies the simplest compounds and can be arbitrarily extended to include the more complex compounds. The system of halocarbon nomenclature, or halon numbers, used in this report is explained in detail in Appendix B.

5. Mechanism of Combustion and Fire Extinguishment. The mechanism of combustion in Class B fires involves oxidation reactions in the vapor phase at elevated temperatures. Before a liquid can burn, it must be converted to a gas or vapor. Easily combustible liquids vaporize sufficiently at normal temperatures to provide a vapor film of combustible concentration at the liquid surface. Heavy oils can be ignited only after the heat has vaporized enough of the oil to initiate combustion.

The mechanism of combustion in Class A fires is in part similar to that of Class B fires. A solid (wood, for example) may partially decompose under applied heat, and the gases produced on decomposition may then undergo combustion. In a wood fire, the solid residue after thermal decomposition (charcoal) may undergo direct combustion, a fact demonstrated by the presence of embers in Class A fires.

Class C fires may be combinations of Class A and B fires, so that the same generalizations may be made concerning this type. A Class C fire is considered apart from the first two classes, since the presence of an electrical potential requires an electrically non-conductive extinguishing agent.

Classically, a fire may be extinguished in one of three ways: by exclusion of oxygen, by removal of the combustibles, or by removal of heat. In the past, the action of such agents as carbon dioxide or methyl bromide has been considered to be a result of excluding oxygen from the burning material. But, if exclusion of oxygen were the sole mechanism of fire extinguishment, one inert gas would show little advantage over an equal volume of another gas in putting out a fire. Thus, some other factor must be present in the fire extinguishing action of such agents as carbon dioxide and methyl bromide, and this factor must logically involve the removal of heat or energy from the reacting gases. The quantitative effect of this latter factor determines the effectiveness of a chemical agent. (For a brief theoretical discussion of flame extinguishment, see Appendix C.)

II. INVESTIGATION

6. General. The criteria used to judge the suitability of a fire extinguishing agent for a small hand unit are derived principally from the military characteristics (see Appendix A). They include fire extinguishing effectiveness, corrosiveness, toxicity, electrical conductivity, volatility, freeze point, cost, and commercial availability.

In the small portable units it is desired to have vaporizing liquids (from the standpoint of minimum damage to equipment) since after extinguishment, the vaporizing liquid leaves no residue. Previously, agents otherwise suitable for use in small, hand-portable units have not been entirely satisfactory at low temperatures, and, in addition, have displayed varying degrees of toxicity. These agents and their characteristics are summarized in Table I. Since it had been noted that among the various fire extinguishing agents, the halocarbons and halohydrocarbons possessed the desired qualities of volatility and vaporization without the deposition of a residue, these and similar halogen compounds were selected for study and research. Also, since the principal aim of this investigation was to produce an agent less toxic and corrosive than carbon tetrachloride and more effective than methyl bromide, and because of the inherent inertness, low toxicity, and stability of certain fluorocarbons¹ it was desired to include compounds of this type in the research and study. However, it was noted that the synthesis of fluorine compounds required special techniques and "know how" not present in other halogen work. A survey of the field of fluorine chemistry revealed that the Purdue Research Foundation was qualified to undertake this research. (The Foundation had become prominent in this field as a result of its work for the Manhattan District.)

Following negotiations and contacts with other qualified organizations, contract W-44-009 eng-507 was initiated with the Foundation in June 1947. This work is being conducted according to the program indicated below.

a. Laboratory tests of fire extinguishing effectiveness, including studies of such variables as type of fuels used, and studies of critical data (boiling and freezing point).

b. Laboratory investigations and study of other physical and chemical properties such as toxicity, corrosiveness, electrical conductivity, determination of thermal decomposition products.

c. Engineering tests of fire extinguishing effectiveness at normal and at reduced temperatures.

1. When two or more fluorine atoms are attached to a carbon atom in a compound the result is distinct inertness.

Table I. Fire Extinguishing Agents in Use

Agent	Application (Class of Fire)			Limitations and Remarks
	A	B	C	
Water	X			Freezes at 32 F; causes some damage in use.
Chemical foam	X	X		Not adaptable for use at low temperatures. Use occasions considerable inconvenience, and may cause damage.
Soda-acid (essentially self-propelling water type)	X			Freezes at between 25 and 30 F; has corrosive action; causes some damage in use.
Dry powder types		X	X	Military application of dry powder type investigated at ERDL; dry powder found to leave a copious residue which can injure fine machinery. (a)
Carbon tetrachloride (halon 104)		X	X	Freezes at 7.6 F, and must be winterized; otherwise only a moderately effective agent. Presents toxic hazards (especially dangerous when fire is in confined, unventilated location), but is not as toxic as methyl bromide, and has negligible corrosive action when inhibited with CS ₂ .
Chlorobromomethane		X	X	Boiling point 156 F; presents toxic hazards (especially when fire is in confined, unventilated location, but is not as toxic as methyl bromide; otherwise, an effective agent.
Carbon dioxide		X	X	Solidifies on attempted discharge at -65 F. May be winterized by addition of N ₂ ; however, even when winterized, extinguishers are not entirely reliable. Concentrations above 10% have physiological effects leading to unconsciousness.
Methyl bromide (halon 1001)		X	X	Presents serious toxic hazards otherwise, an effective agent.

(a) ERDL Report 1143, Dry Powder Fire Extinguishers, 23 September 1949.

d. Final container design.

e. Development of sources of supply for agent and containers.

f. Service testing.

This report covers technical phases a, b, and c to 1 April 1950, and the material is presented here in the same general order.

Sources of supply have been developed where possible, and continued liaison has been maintained with interested manufacturing concerns.

Much of the work conducted at Purdue concerned original syntheses of some of the compounds evaluated. That work is not covered in this report, but will be presented in the chemical literature by the personnel responsible for the syntheses.

7. Laboratory Investigation of Flame Extinguishment. It became evident shortly after the initiation of studies at the Purdue Research Foundation that the laboratory investigation of flame extinguishment should be resolved into an investigation of the flame inhibition of various agents on a hydrocarbon vapor, and corollary investigations of the effects of different combustibles, binary mixtures of agents, temperature, and pressure. To facilitate interpretation of the flame inhibition data obtained at Purdue, a test was developed in the ERDL Materials Laboratory to determine the effect of selected agents on small laboratory fires involving a hydrocarbon, normal heptane. These laboratory investigations are presented in greater detail in the following subparagraphs.

a. Flame Inhibition Tests Conducted by the Purdue Research Foundation. An extensive literature search revealed that previous testing of compounds used as fire extinguishing agents had been conducted on an empirical basis under such varying conditions that the results from the different types of tests could not be compared.

The PRF concluded that a test procedure should be used that would render reproducible results, be applicable to a number of different compounds, require only a small amount of compound to be evaluated, and be conveniently operated. Consequently, they adopted a procedure used by the Bureau of Mines to investigate flammable limits of various fuels and the effect of certain inert gases on these limits.

The method evaluates the flame inhibition properties of inert gases or vapor on mixtures of a combustible vapor

and air, and consists of determining whether or not a given mixture of the three components can be ignited by a spark gap.² For a given agent a number of determinations are made with varying mixtures, and the instances of flame propagation or nonpropagation and the concentrations of the components are recorded. (The apparatus and procedures with which this was done are described in Appendix D, Exhibit 1.)

The data obtained in these tests were expressed graphically, the volume percentage of the agent being plotted against that of the combustible vapor. Different symbols were used to represent points corresponding to propagation and nonpropagation of flame respectively, so that the boundary between these two areas could be determined and drawn as a curve. Thus, any point within the flammable area defined by the curve represents a concentration of combustible and agent vapor that will propagate flame.

A sample data sheet showing the evaluation of methyl bromide (halon 1001) is presented in Table II. From similar data sheets the flammability curves of all the compounds were plotted, and the coordinates of their flammability peaks were obtained. During the later part of the investigation flammability determinations were made only in the region of the peaks to eliminate some of the numerous trials necessary to completely define the entire curve.

It is seen in Fig. 1 that a peak in the flammability area occurs at 1.4 percent n-heptane and 9.7 percent methyl bromide in the air - n-heptane - methyl bromide mixture. This peak is the minimum concentration of agent in the combustible mixture that will inhibit flame propagation for any concentration of the combustible

2. In the experimental determination of the flammability peaks the spark gap was located at the bottom of the combustion tube so that when a flame was propagated it traveled in an upward direction. A discussion of the effect of direction of the flame propagation on flammable limits has been presented by Coward and Jones (H. F. Coward and G. W. Jones, Limits of Inflammability of Gases and Vapors, U. S. Department of the Interior, Bureau of Mines, Bulletin 279, Washington, U. S. Government Printing Office, 1939, p.2). It has been noted by independent investigators that downward propagation is less apt to occur in mixtures near the limits of flammability, and that results are somewhat more reproducible. With upward flame propagation the traverse of the flame is aided by convectional currents above the flame front, so that a greater amount of inhibitor will be needed to insure non-combustion in all concentrations of combustible and air. Thus, as far as the individual agent is concerned, upward propagation affords a more rigorous test.

Table II. Flammable Limits for Mixtures of N-Heptane,
Air, and Methyl Bromide (Halon 1001)

Pressure, (mm, Hg)			Volume %		Result(a)
n-C ₇ H ₁₆	CH ₃ Br	Total	n-C ₇ H ₁₆	CH ₃ Br	
6.0	20.0	498	1.2	4.0	-
7.0	20.0	508	1.4	3.9	+
6.0	40.0	500	1.2	8.0	-
7.0	40.0	500	1.4	8.0	+
10.0	43.0	500	2.0	8.6	+
10.0	44.0	501	2.0	8.8	-
15.0	27.0	500	3.0	5.4	+
15.0	30.0	499	3.0	6.0	-
17.0	25.0	500	3.4	5.0	-
16.0	25.0	504	3.2	5.0	+
13.0	35.0	498	2.6	7.0	-
12.0	35.0	500	2.4	7.0	+
11.0	40.0	501	2.2	8.0	-
10.0	40.0	501	2.0	8.0	+
8.0	46.0	501	1.6	9.2	+
8.0	47.0	499	1.6	9.4	-
7.0	48.0	501	1.4	9.6	+
7.0	49.0	500	1.4	9.8	-
25.0	9.0	503	5.0	1.8	+
26.0	9.0	503	5.2	1.8	-

(a) + indicates that the mixture burned.
- indicates that the mixture did not burn.

material, and is consequently taken as a criterion of the effectiveness of the inert vapor in inhibiting flame propagation. The flammability peak criteria may be compared to determine the relative values of various agents on the volume basis. For example, methyl bromide (halon 1001) with a flammability peak at 9.7 percent in n-heptane and air is superior, volume for volume, to carbon dioxide with a flammability peak at 29.5 percent under the same condition; that is, the volume of methyl bromide vapor required to inhibit flame propagation in a given volume of combustible gas mixture would be one-third that required if carbon dioxide were used.

Table III summarizes the results of the flame inhibition studies, and presents the melting and boiling points of the various compounds, where available. In the table, the compounds are arranged in the descending order of effectiveness on a vapor-volume basis, and the coordinates of the flammability peaks (concentrations in volume percentage for both fuel and agent) are presented.

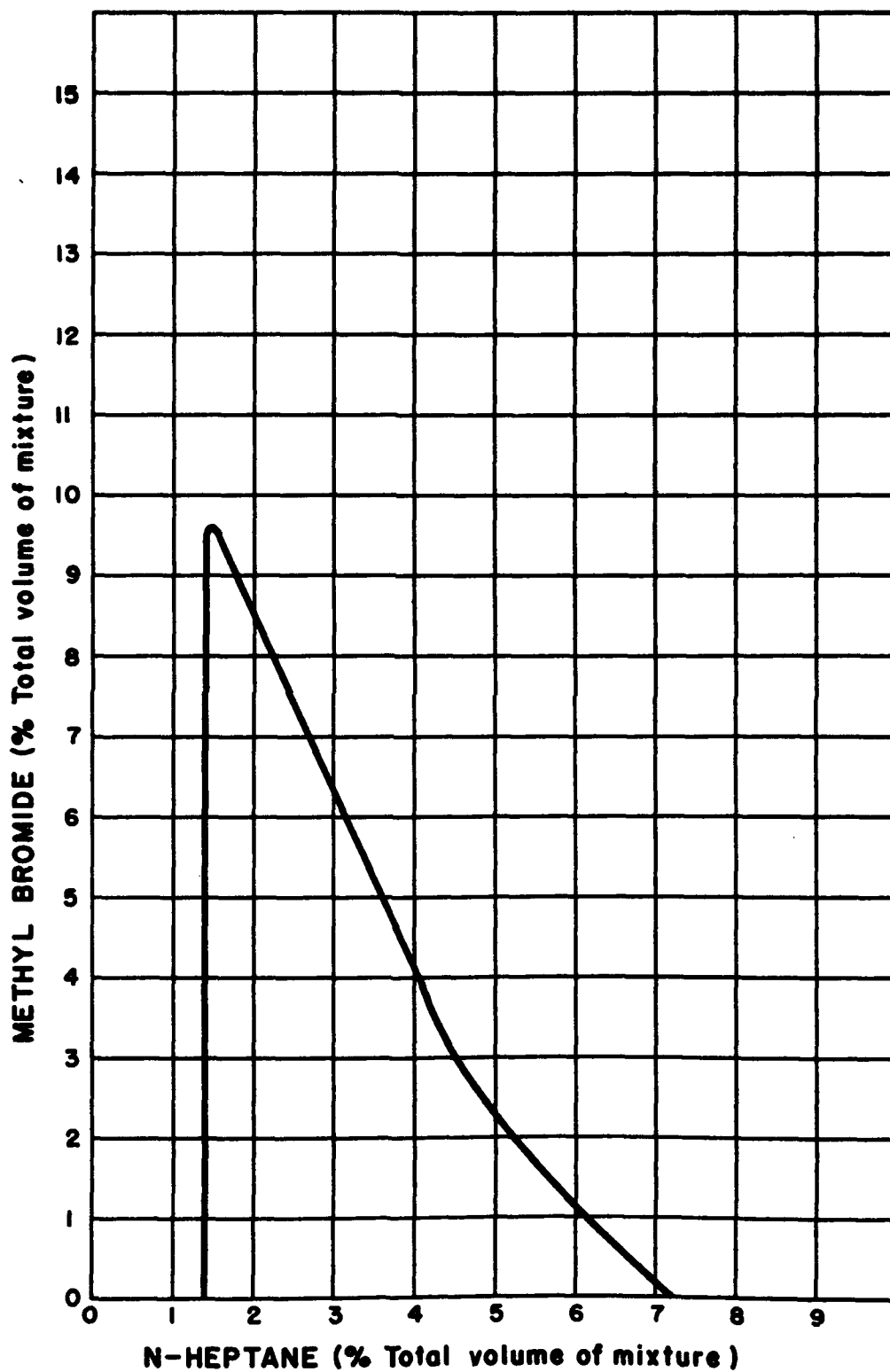


Fig. 1. Flammability curve for methyl bromide (halon 1001) in a mixture of N-heptane and air.

The laboratory flame extinction and inhibition data were collected on a vapor volume basis because it was the most convenient method. However, to provide a means of evaluating the agents on a practical basis, it was necessary to express their fire extinguishment effectiveness in terms of a percentage based on the weight of the agent used (see column 9, Table III). For this purpose the following formula was used (methyl bromide is taken as the criterion, since one goal of the project was to develop an agent superior to it in effectiveness):

$$E = \frac{V_o M_o}{V_a M_a} (100)$$

Where E = Percentage weight effectiveness (methyl bromide being 100%)

V_o = Volume percent of methyl bromide at its flammability peak with n-heptane as the fuel

V_a = Volume percent of agent at its flammability peak with n-heptane as the fuel

M_o = Formula weight of methyl bromide

M_a = Formula weight of agent

b. Flame Extinguishment tests Conducted at ERDL Materials Branch. Over 60 different compounds were evaluated by the flame inhibition method at PRF. It was realized, however, that the flame inhibition method of screening compounds with respect to fire extinguishing effectiveness was open to some question, i.e., from the flame inhibition tests at agent concentrations where no flame was propagated, it could not be safely assumed that the given agent concentrations could extinguish a flame which had been initiated before application of the agent. To remove any doubt concerning the interpretation of the data, a series of tests were made by the ERDL Materials Branch in which inert vapors (various halogen compounds and carbon dioxide) were applied to small n-heptane fires under closely controlled conditions. These tests were not designed to check the flammability peak data of individual compounds tested at Puréne, but to determine if the relative effectiveness of various agents as indicated by the flame inhibition method was valid for the agents when applied to the n-heptane pot fires in the laboratory. (The apparatus and procedure for these tests are presented in Appendix D, Exhibit 2.)

Table IV presents the summarized results of the laboratory fire tests. The values presented in the "Time" column represent the average of several determinations at the flow rate

Table III. Summary of Compounds Evaluated as Fire Extinguishing Agents at the EBF.^a

Agent (1)	Chemical Formula (2)	Molar Wt. (3)	Molecular Weight (4)	Boiling Point (°C) (5)	Boiling Point (°F) (6)	Concentration at Peak Flammability (% by Vol.) (7)	Weight Effectiveness (% by Vol.) (8)	Remarks (9)	
Dibromodifluoromethane	CH ₂ Br ₂	186	186	84.5	...	4.4	4.8	107	
Trichlorofluoromethane	CHCl ₃	119.5	119.5	10.7	...	3.0	4.3	81	
1,1,1-trichloro-2,2,2-trifluoroethane	CHCl ₃ CF ₃	299.4	299.4	95	...	3.4	4.3	95	
1,1,1-trichloro-2-chloro-2-trifluoroethane	CHCl ₃ CClCF ₃	351.2	377	98-99	...	3.3	4.6	73	
2-bromo-1,1,1-trifluoroethane	CH ₂ BrCF ₃	236.9	177	48.6	...	3.3	4.9	106	
1,1,1-trichloro-2-trifluoroethane	CHCl ₃ CF ₃	299.4	260	46.4	-112	3.3	4.9	78	
1,1,1-trichloro-2,2,2-trifluoroethane	CHCl ₃ CF ₃	299.4	354	118	...	3.3	5.0	98	
Dibromomethane	CH ₂ Br ₂	100	176	98.5	-20.8	8.1	3.0	100	
Isopropyl bromide	CH ₃ CH ₂ CH ₂ Br	150.0	246	36-37.5	...	3.0	3.3	70	
2-bromo-1,1,1-trifluoroethane	CH ₂ BrCF ₃	236.9	177	68	...	1.3	3.4	96	
Ethyl iodide	CH ₃ CH ₂ I	226.0	156	70.2	-165	8.3	3.6	105	
Bromodifluoromethane	CH ₂ BrF ₂	171.9	159	-85	...	4.0	6.1	76	
Methyl iodide	CH ₃ I	140.9	148	42.4	-44.4	8.1	6.1	106	
Bromotrifluoromethane	CHBrF ₂	136.9	149	-60	...	3.0	6.1	101	
Ethyl bromide	CH ₃ CH ₂ Br	109.0	109	38.4	-117.8	8.3	6.8	136	
1-bromo-2,2,2-trifluoroethane	CH ₂ BrCF ₃	236.9	159	76	...	8.3	6.3	92	
2-bromo-1-chloro-1,1,1-trifluoroethane	CHClBrCF ₃	241.9	194	90	...	1.3	6.4	74	
Dibromofluoromethane	CHBr ₂ F	136.9	158	65	...	3.4	6.4	75	
2-bromo-1,1,1-trifluoroethane	CH ₂ BrCF ₃	236.9	165	86.5	...	3.4	6.8	85	
Perfluoro(ethyl)acetone	C ₄ F ₁₀ O	238.0	400	99.5	...	3.4	6.8	34	
Perfluoro(1,3-dimethylisobutylene)	C ₆ F ₁₄	338.0	400	108	...	3.4	6.0	34	
Isobutyl bromide	CH ₃ CH ₂ CH ₂ CH ₂ Br	170.0	246	-88.5	...	8.3	6.8	69	
Perfluoro(1,3-dimethylisobutylene)	C ₆ F ₁₄	338.0	400	101	...	3.4	6.8	34	
1-bromo-2-chloroethane	CH ₂ BrCH ₂ Cl	126.9	144	106.7	-16.6	1.7	7.9	89	
2-bromo-1-chloro-1,1,1-trifluoroethane	CHClBrCF ₃	241.9	180	68	...	3.0	7.0	71	
Perfluoro(methyl)acetone	C ₄ F ₁₀ O	238.0	350	75-76	-82	3.0	7.5	35	
Perfluorobutane	C ₄ F ₁₀	238.0	368	82.4	...	3.0	7.5	38	
Chlorobromomethane	CH ₂ BrCl	106.9	130	68-69	-88	8.8	7.6	94	
Bromodifluoromethane	CHBr ₂ F	136.9	131	-14.5	...	4.0	8.4	84	
1,1,1-trichloro-2-trifluoroethane	CHCl ₃ CF ₃	299.4	375	107.5	47.6	-35.4	4.0	9.0	55
Hydrogen bromide	HBr	81	81	-67	-86	4.0	9.3	102	
Bromochlorodifluoromethane	CHBrClF ₂	161.9	166	-6	...	3.0	9.3	60	
Methyl bromide	CH ₃ Br	94.9	95	4.5	-25	1.4	9.7	100	
Difluoromethyl bromide	CH ₂ BrF ₂	136.9	143	-66	...	8.6	9.7	66	
Perfluorobutane	C ₄ F ₁₀	238	258	-1.7	...	3.4	9.8	39	
Silicon tetrachloride	SiCl ₄	169.9	170	57.6	-70	3.0	9.9	35	
1,1,1-trichloro-2-trifluoroethane	CHCl ₃ CF ₃	299.4	171	3.6	-94	3.0	10.8	50	
Carbon tetrachloride	CCl ₄	154	154	76.8	-88.6	3.2	11.5	58	
2-chloro-1,1,1-trifluoroethane	CH ₂ ClCF ₃	236.9	135	30	...	1.0	12.0	58	
3-chloro-1,1,1-trifluoroethane	CH ₃ CHClCF ₃	250.4	135	45	...	0.7	12.2	57	
Chlorotrifluoromethane	CHClF ₂	131	109	-82	-180	3.3	12.3	71	
Bromotrifluoromethane	CHBrF ₂	86	138	-78	-183	3.0	13.4	50	
Dichlorodifluoromethane	CHCl ₂ F ₂	122	182	-30	-226	3.9	14.9	51	
Chloroform	CHCl ₃	105	180	61.2	-45.5	3.6	17.5	44	
Trifluoromethane (Fluorocarbon)	CHF ₃	70	70	-82.2	-165	8.5	17.8	74	
Chlorodifluoromethane	CHClF ₂	121	87	-40	-107	8.3	17.9	59	
Octafluorocyclopentane	C ₅ F ₁₀	238(c)	800	-5	-46	8.5	18.1	85	
Sulfur hexafluoride	SF ₆	...	146	-65.8	-90.8	4.2	20.5	51	
Boron trifluoride	BF ₃	...	68	-101	-187	4.0	20.5	66	
Phosphorus trichloride	PCl ₃	...	138	75.9	-111.8	...	22.5	30	
Hydrogen chloride	HCl	...	36.5	-85	-111	3.0	25.5	92	
Carbon tetrachloride	CCl ₄	14	88	-146	-184	1.8	26	40	
Carbon dioxide	CO ₂	...	44	...	-78.5 ^b	2.7	29.5	71	
Hydrofluoromethane (H, 2-chloro-1-propylene)	(C ₂ H ₃) ₂ ClF	...	421	28.5	...	
Water	H ₂ O	...	18	100	0	...	28	...	
Dichloromethane	CH ₂ Cl ₂	100	85	40-41	-96.7	...	flam.	...	
Bis(trifluoromethyl)-benzene	C ₆ H ₂ (CF ₃) ₂	...	214	116-117	-15	...	flam.	...	
(Trifluoromethyl)-benzene	C ₆ H ₅ CF ₃	...	146	128.5	-25	...	flam.	...	
Nitrogen trifluoride	NF ₃	...	71	-110	-810	...	unstable	...	
Tetrafluoroethylene	CF ₂ =CF ₂	...	100	-76.3	-108.5	...	flam.	...	
1-bromopropane	CH ₃ CH ₂ CH ₂ Br	200.4	125	70.8	-109.9	...	flam.	...	
Vinyl bromide	CH ₂ =CHBr	...	95	15.8	-158	...	flam.	...	
Bromine	Br ₂	...	160	58.7	supported combustion	Extinguishing agent	
2-bromopropane	CH ₃ CHBrCH ₃	...	121	16	flam.	...	

(a) The flammability data are taken from the EBF Progress Report for the Period 1 September 1949 to 30 February 1950. Molecular and atomic weights are indicated to the nearest unit, and the weight effectiveness is based on the methyl bromide = 100.
(b) Solubility.

indicated. A moderate variation in the flow rate did not appear to cause an equivalent change in the volume of agent necessary to extinguish the laboratory fires.

c. Study of Binary Mixtures at PRF. Although the goal of this project was to develop, if possible, a single agent that would meet all the military requirements, the PRF noted that there was a possibility that a mixture of two or more agents would meet the requirements. For this reason, a limited study was conducted to determine fire extinguishing effect of mixtures of two agents. This was done by determining the flammability peaks of n-heptane in the presence of equi-volume mixtures of various halogen compounds, and also by varying the proportions of two agents at a fixed concentration of the combustible. A notation was made of those combinations and concentrations of selected agents in binary mixtures that displayed synergistic, as synergistic, or antiennergistic effects, that is, whether or not a binary mixture was more effective, as effective, or less effective than the molar average effectiveness of the components.

Table IV. Summary of Data for Compounds Evaluated
in Laboratory Fire Tests at the ERDL

Compound	Chemical Formula	Halon No.	Flow Rate (l/min.)	Extinguish-ment Time (sec.)	Volume Required (liters)	Weight Effect-iveness (%)
Methyl bromide	CH ₃ Br	1001	4.4	6.3	0.46	100 ^a
			5.8	5.4	0.52	
Dichlorodi-fluoro-methane	CCl ₂ F ₂	122	5.2	13.8	1.2	29 ^a
			6.5	12.0	1.3	
Bromodi-fluoromethane	CHBrF ₂	1201	3.8	6.6	0.41	85 ^a
			5.0	5.1	0.43	
Bromotri-fluoromethane	CBrF ₃	1301	3.5	5.8	0.22	130 ^a
			4.7	3.4	0.26	
Sulfurhexa-fluoride	SF ₆	..	5.7	21.3	2.0	16
Carbon dioxide	CO ₂	..	12.2	11.6	2.4	44 ^a
			12.8	11.8	2.5	
Carbontetra-fluoride	CF ₄	14	9.1	15.7	2.3	23
Chlorotri-fluoromethane	CClF ₃	131	5.6	6.5	0.60	74

(a) Average of two determinations.

Table V presents flammability peaks for equivalent binary mixtures of dibromomethane and selected agents, the flammability peak of the former being 5.2 percent. The calculated flammability peak of the mixture is an average of the observed flammability peaks of the respective agents.

Table VI presents the effects of various binary mixtures of agents in suppressing the flammability of fixed concentrations of n-pentane fuel (2.5, 4.0 and 6.0 percent by volume). In obtaining the data, the proportion of the agents in the binary mixture were varied for a given fuel concentration. The percentages of agents in the binary mixtures are on a volume basis.

Table V. Effect of Equivalent Mixture of Dibromomethane and Selected Agents on the Flammability of Air and n-heptane

Selected Agent	Chemical Formula	Halon No.	Concentration at Flammability Peaks (% by Vol.)			Effect
			Agent Obs.	Mixture		
				Obs.	Calc.	
Tribromo-fluoro-methane	CBr_3F	1103	4.3	5.3	4.8	Antiennergistic
Perfluoro-ethylcylo-hexane	$\text{C}_6\text{F}_{11}\text{C}_2\text{F}_5$	HP(E)	6.8	5.4	6.0	Synergistic
Ethyl bromide	$\text{CH}_3\text{CH}_2\text{Br}$	2001	6.2	5.7	5.7	Asynergistic
Carbon tetra-chloride	CCl_4	104	11.5	7.2	8.4	Synergistic
Chloroform	CHCl_3	103	17.5	9.3	11.4	Synergistic

d. Study of the Effects of Various Combustibles at PRF.

In the tests of flame inhibition, n-heptane was selected as the combustible, since it is a typical straight chain hydrocarbon and possesses sufficient volatility. To demonstrate, from the standpoint of combustible material, the significance of the tests with n-heptane, a study was made to determine if the relative effectiveness of an agent varied appreciably when applied to different combustibles. The study was carried out by determining the flammability peaks of various agents in the combustible vapors of acetone,

Table VI. Effect of Binary Mixtures of Halogen Compounds on the Flammability of Air and N-pentane, at Selected N-pentane Concentrations

Agents in Binary Mixture	Concentration of N-pentane in Total Mixture (% by Vol.)	Effect (Deviation from Direct Mean) at Indicated Concentrations of Agent in the Binary Mixture
Methyl bromide and sulfur hexafluoride	2.5	At concentration of SF_6 above 40%, synergistic; at other concentrations, antiennergistic
	4.0	Entire range synergistic
	6.0	Entire range synergistic
Methyl bromide and perfluorobutane	2.5	Entire range antiennergistic
	4.0	Entire range synergistic
	6.0	Entire range synergistic
Methyl bromide and ethyl bromide	2.5	Entire range antiennergistic
Methyl iodide and ethyl bromide	2.5	At concentrations of $\text{C}_2\text{H}_5\text{Br}$ above 65%, synergistic; at other concentrations, antiennergistic
	4.0	Entire range synergistic
	6.0	Entire range synergistic
Dichloromethane and ethyl bromide	2.5	Entire range synergistic
	4.0	Entire range synergistic
	6.0	Entire range synergistic
Chlorotrifluoromethane and ethyl bromide	2.5	At concentrations of CClF_3 above 55%, synergistic; at other concentrations, antiennergistic
	4.0	At concentrations of CClF_3 above 40%, synergistic; at other concentrations, antiennergistic
	6.0	At concentrations of CClF_3 above 75%, synergistic; at other concentrations, antiennergistic
Carbon tetrachloride and trichloroethylene	2.5	At concentrations of CCl_4 from 0 to 36%, antiennergistic; above 36%, synergistic
	4.0	At concentrations of CCl_4 from 0 to 36% synergistic; from 36% to 70%, antiennergistic
	6.0	At concentrations of CCl_4 from 0 to 36%, synergistic; from 36% to 70%, antiennergistic

benzene, diethyl ether, ethyl acetate, ethyl alcohol, and isopentane.

The flammability peaks of selected agents in various combustible solvents are shown in Table VII, expressed as volume percent of the inhibiting agents at the maxima of the flammability curves.

e. Study of the Effect of Temperature and Pressure at PRF. The bulk of the flame inhibition tests were carried out at room temperature; however, since an agent was desired which would be effective over a wide temperature range, a series of tests were made to determine the flammability peak at -78 C, 27 C, and 145 C (-108 F, 81 F, and 293 F respectively) so that any temperature effect might be noted. The procedures and apparatus employed are described in Appendix D, Exhibit 3. These temperatures were selected for experimental convenience, and isobutane was selected as the combustible, since it possessed better volatility at reduced temperatures than n-heptane. The coordinates of the flammability peaks are presented in Table VIII, and the curves in Appendix D, Exhibit 4.

The flammable areas at -78 C were quite irregular. Chlorotrifluoromethane (halon 131) showed divided areas, and the other compounds showed sharp indentations in the flammable areas (see Appendix D, Exhibit 4). The data concerning pressure are at present incomplete.

Originally a copper combustion tube had been constructed for the PRF studies at reduced temperatures. A port was constructed at the top of the tube so that the flame would not be visible unless it traveled all the way up the tube, the apparatus being otherwise similar in design and dimensions to the glass set-up used for flammability determinations at normal temperature. When mixtures of n-heptane and air were evaluated in the copper tube it was found that the limits of flammability corresponded very closely to those found using glass tubes. However, when methyl bromide was added to the mixture, the peak in the flammability curve was found at about 1.5 percent agent, as compared to 9.7 percent in glass tubes, indicating that the presence of copper enhanced the action of methyl bromide.

8. Laboratory Investigation of Corrosion at PRF. Since the agent would be subject to storage under any climatic conditions for long periods of time in a metal container, stability to metals was chosen as a means of classifying the materials. Preliminary studies at PRF showed that the compounds being evaluated were, in general, stable to powdered aluminum at reflux temperatures. Accordingly, a series of experiments were conducted in which the test compounds were heated in contact with strips of metal at 392 F (200 C). In

Table VII. Effect of Various Combustibles on Flammability of Mixtures of Halogen Compound, Air, and Fuel

Combustible	Chemical Formula	Concentration of Agent at Flammability Peak (% by Vol.)					
		CBrF_3 (Halon 1301)	CH_2Br_2 (Halon 1002)	$\text{C}_2\text{H}_5\text{Br}$ (Halon 2001)	CH_3Br (Halon 1001)	SF_6 (-- --)	CF_4 (Halon 14)
n-heptane	C_7H_{16}	6.1	5.2	6.2	9.7	20.5	26
Isopentane	C_5H_{12}	6.3	6.8	6.3	8.4	19.8	20.4
Benzene	C_6H_6	4.3	7.3	8.2	8.4	18.3	23.6
Ethyl alcohol	$\text{C}_2\text{H}_5\text{OH}$	3.7	5.7	5.2	6.2	10.6	19.8
Diethyl ether	$(\text{C}_2\text{H}_5)_2\text{O}$	6.3	7.7	7.3	7.2	21.8	22.4
Acetone	$(\text{CH}_3)_2\text{CO}$	5.3	5.7	5.8	7.3	16.4	18.7
Ethyl acetate	$\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$	4.6	4.3	6.3	6.8	17.5	21.4

Table VIII. Effect of Temperature on the Flammability Peak of Halogen Compounds with Isobutane (C_4H_{10}) and Air

Agent	Formula	Halon No.	Concentration at Peak Flammability (% by Vol.)					
			at -78 C		at +27 C		at +145 C	
			Agent	C_4H_{10}	Agent	C_4H_{10}	Agent	C_4H_{10}
Bromotrifluoromethane	CBrF_3	1301	3.25	4.5	4.7	4.6	7.3	4.0
Methyl bromide	CH_3Br	1001	3.75	3.5	6.75	4.0	8.3	4.0
Chlorotrifluoromethane	CClF_3	131	8.25 ^a	3.5	10.75	4.25	12.8	4.0
Sulfur hexafluoride	SF_6	--	12.75	5.0	15.75	5.0	17	5.5
Carbon tetrafluoride	CF_4	14	18.25	5.0	23.75	4.0	21.4	3.5

^a Divided flammable area noted, lower peak at 2.0

general, only the materials boiling above about 50 C were used in this study and these compounds were chosen to show the effects, if any, of structural relationships on instability. The apparatus and procedures used in this test are described in Appendix D, Exhibit 5.

The data of the corrosion tests are summarized in Table IX. The compounds have been divided into four groups, according to the weight change in the metal. The results show that the compounds are less stable toward aluminum than to either brass, copper, iron or magnesium, but that there appears to be no significant difference between the stability of these compounds to brass and copper. Complete reports of corrosion tests are found in Appendix D, Exhibit 6.

9. Electrical Conductivity Tests at PRF. One of the military requirements of the new type agent is that it be suitable for application to Class C fires; that is, it must be essentially a nonconductor of electricity. In view of this, the PRF undertook appropriate resistivity measurements. A Westinghouse power factor cell and General Radio megohm bridge, Type 544-B, were used in determining the volume resistivities of various fluorocarbons as listed below:

<u>Compound</u>	<u>Resistivity</u> (Ohm-cm)
Perfluoromethylcyclohexane	4×10^{14}
Perfluoroethylcyclohexane	1×10^{11}
Perfluoroindane	2×10^{14}
Perfluoro-n-heptane	2×10^{12}
Perfluoronaphthalane	4×10^{13}

These results indicated that the compounds are, for practical purposes, nonconductors. Data on the bromofluorocarbons are at present incomplete.

10. Laboratory Investigation of Toxicity. An investigation of toxicity was started at the Army Chemical Center (1) to determine the approximate lethal concentrations of selected new agents and of such agents as chlorobromomethane (halon 1011) and carbon tetrachloride (halon 104); (2) to conduct a thorough study of the long-term physiological effects of the finally selected agent or agents; and (3) to conduct toxicity tests in the presence of flame to determine the physiological effects of the selected agents under simulated conditions of application. The detailed planning of this program has been conducted in cooperation with both the Army Industrial Hygiene Laboratory and the Medical Division of the Army Chemical Center.

Table IX. Stability of Halogen Compounds after 30-day
Contact with Metals at 200 F and 392 F

Compound	Weight Change at Indicated Temperatures									
	Aluminum		Brass		Copper		Iron		Magnesium	
	392 (F)	200 (F)	392 (F)	200 (F)	392 (F)	200 (F)	392 (F)	200 (F)	392 (F)	200 (F)
<u>Halocarbons</u>										
C ₇ F ₁₆	B	...	A	...	A	...	A	A(a)
C ₆ F ₁₁ CF ₃	B	...	A	...	A	...	A	A(a)
C ₆ F ₁₁ CF ₂ CF ₃	B	...	A	...	A	...	A	A(a)
1,3-C ₆ F ₁₀ (CF ₃) ₂	B	...	A	...	A	...	A	A(a)
1,4-C ₆ F ₁₀ (CF ₃) ₂	B	...	A	...	A	...	A	A(a)
C ₁₀ F ₁₈	D	A	...	A	A(a)
CCl ₂ FCClF ₂	A	C	...	A	B(b)
CBrF ₂ CBrF ₂	D	A	...	A	C	A	A	A
CF ₂ ICF ₂ I	...	C(b)	...	B(b)	B(b)
CCl ₄	B	C	...	B	D	B	B	B
<u>Halohydrocarbons</u>										
CF ₃ CH ₂ CH ₂ Br	A	B	...	B
CF ₃ CHBrCH ₃	D	A	B	A	C	A	B	A
CH ₂ BrCF ₂ CH ₂ Br	...	A(c)	...	A(c)	B(c)	...	B(c)
CH ₂ BrCH ₂ Cl	C	D	...	A	C	B	C	B	...	B
CH ₂ BrCl	C	D	...	B
CH ₂ Br ₂	C	D	...	C
CH ₂ Cl ₂	B	D	...	B
CH ₃ CH ₂ Br	...	C(d)	...	B(d)	C(d)	...	B(d)
CH ₃ CH ₂ I	...	C(d)	...	B(d)	C(d)	...	B(d)

Code: A - Weight change less than 0.01g.
 B - Weight change between 0.01 and 0.1g
 C - Weight change greater than 0.1g
 D - Completely consumed
 (Original weight of all samples varied
 from 1.2 to 3.5 g, depending on the
 metal used.)

Notes: (a) contact time
 27 days
 (b) contact time
 14 days
 (c) contact time
 32 days
 (d) contact time
 11-15 days

To date only screening tests have been conducted at the Army Chemical Center. The method used for these tests was adapted from the procedure used by Deichman and Mergard in their study of approximate lethal doses (ALD) of various compounds. In the tests, white rat specimens were exposed to various vapor concentrations of the agent for a period of fifteen minutes in order to determine the approximate lethal concentration (ALC) of the agent.³ (For a description of the procedure used to bracket the ALC see Appendix D, Exhibit 7.)

The toxicity of the natural vapors and of the pyrolyzed vapors of the same agents are presented in Table X. The specimens were observed for 14 days after the 15-minute exposure, and the toxicities recorded are based on mortalities occurring in the 14-day period. In the tests with pyrolyzed vapors, the vapors were passed with air through an iron pipe heated to 800 C, and subsequently cooled to room temperature. This test was conducted to obtain preliminary indications of the toxic effect of the agents when applied to fires with hot metal (iron) surfaces involved. Except for the use of the hot iron tube the same procedures were used to obtain these data as were used to screen the direct toxicities.

11. Practical Fire Tests. In order to verify the findings of the laboratory studies, and to make a final screening of the compounds displaying superior fire extinguishing effectiveness, practical tests were conducted on Class A and Class B fires with the following agents:

<u>Agent</u>	<u>Halon No.</u>
Bromotrifluoromethane	1301
Dibromodifluoromethane	1202
Dibromotetrafluoroethane	2402
Perfluoromethylcyclohexane	GN(M)
Methyl bromide	1001
Carbon tetrachloride	104
Carbon dioxide	..
Methyl iodide	10001
Chlorobromomethane	1011

3. The ALC is used to indicate the toxicity of the agent when it is inhaled. The term is analogous to ALD, which indicates the toxicity of the agent when it is administered orally or subcutaneously, and is derived in the same manner.

Table I. Approximate Lethal Concentrations for 15-minute Exposure to Vapors of Various Fire Extinguishing Compounds

Agent	Formula	Nelson No.	Approximate Lethal Concentration				Vapor Pyrolyzed in Iron Tube at 800 C	
			Natural Vapor		Anesthesia Time		Anesthesia Time	
			mg/l	ppm	min. b	min. b	mg/l	ppm
Bromotrifluoromethane	CF_3Br	1301	5075	800,000	1	86	14,000	10
Carbon tetrachloride	CCl_4	14	3220	895,000	2	3220	895,000	2
Bromochlorodifluoromethane	CF_2ClBr	1211	2,200	324,000	4	52	7,650	...
Dibromotetrafluoroethane	CF_2BrCF_2Br	2402	1340	126,000	1½	17	1,600	5
Carbon dioxide	CO_2	...	1180	698,000	1	1200	698,000	½
Perfluoromethylcyclohexane	$C_6F_{11}CF_3$	GN (M)	1175	81,000	5	117	7,500	5
Ethyl bromide	C_2H_5Br	2001	660	148,000	5	75	16,500	5
Dibromodifluoroethane	CF_2Br_2	1202	470	54,000	1	16	1,850	5
Chlorobromomethane	CH_2ClBr	1011	340	65,000	1	20	4,000	10
Dibromochlorotrifluoroethane	$CClFBrCF_2Br$	2312	285	25,000	2	8	700	8
Dibromodifluoroethane	CH_2BrCF_2Br	2202	190	20,700	...	110	12,000	...
Carbon tetrachloride	CCl_4	104	180	28,000	...	2	300	...
Methyl bromide	CH_3Br	1001	23	5,900	...	60	9,600	...
Methyl Iodide	CH_3I	10001	22	3,800	...	350	60,500	...

(a) Based on Tests with white rats by Medical Division, Army Chemical Center.

(b) At indicated Approximate Lethal Concentration

The first two compounds listed, bromotrifluoromethane and dibromodifluoromethane, were selected because the laboratory studies indicated that the most effective and stable agent would be a bromofluorocarbon having a single carbon atom and at least two fluorine atoms per molecule. The second two compounds represent intermediate degrees of effectiveness among new agents studied in the laboratory at the PRF, while the remaining chemicals either represent existing standards or have been proposed in the past as fire extinguishing agents, and have been tested in the studies conducted at the PRF.

Standard Underwriters' Laboratories tests were modified to accommodate 2-pound test samples, 2-foot tub fires being used for the Class B tests and 2- by 2-, 2- by 3-, and 2- by 4-foot cotton waste fire tests for the Class C tests. The procedures for the individual tests are found in Appendix D, Exhibit 8.

In conducting the fire tests it was desired to obtain comparable data on liquid and gaseous agents applied under nitrogen pressure. The pressures used were 800 psi (roughly equivalent to the vapor pressure of CO₂ at room temperature), and 400 psi (an intermediate pressure sufficient to insure discharge at -65 F). At these pressures the agent was discharged as a light mist. For discharging the various agents a Randolph Laboratories standard 2½-pound CO₂ extinguisher was selected because of its simplicity of operation, moderate capacity, and dependability. The human element introduced by the manual attack on the fires combined with such uncontrolled variables as air turbulence to cause deviations from one individual test to another. For most agents as a compromise between a number which would give precise, statistically reproducible results, and the quantity of the new agents available, 10 tests were made and the results were averaged. The time of extinguishment reported gives an indication only of the rate of discharge, and in the times reported there may be varying consistent errors, depending on the individual operator, from one series of tests to another.

The results of the engineering tests are presented in Table XI, in which are tabulated, in addition to the comparative weights of the agents used to extinguish the standard fires, the percent effectiveness of the various agents, based on an assumed value of 100 for methyl bromide. The percent effectiveness (E) was calculated by the following formula:

$$E = \frac{W_m}{W_a} \times 100$$

where W_m = the weight of methyl bromide used in the standard test.

W_a = the weight of agent used in the standard test.

Table XI. Weight Effectiveness, in Percentages, of Selected Agents Against Class B and C Fires (Average of 10 Tests unless Otherwise Noted).

Agent	Formula	Balon No.	Class B 24-in. Test Fire (Agent at 800 psig Initial Discharge Pressure) ^a			Class B 36-in. Test Fire (Agent at 400 psig Initial Discharge Pressure) ^a			Class C 12-in. Test Fire (Agent at 400 psig Initial Discharge Pressure) ^a		
			To Extinguish Avg. Wt. Agent (oz)	Weight Extinguish- ment (g)	Time (sec)	To Extinguish Avg. Wt. Agent (oz)	Weight Extinguish- ment (g)	Time (sec)	To Extinguish Avg. Wt. Agent (oz)	Weight Extinguish- ment (g)	Time (sec)
Dibromodifluoromethane	CF ₂ Br ₂	1202	7.6	148	1.9	6.6	144	1.4	80	5.7	100
Bromotrifluoromethane	CF ₃ Br	1301	7.7	146	3	7.6 ^b	105 ^b	3 ^b	15.6	6.7	186
Carbon dioxide	CO ₂	...	9.1	124	5.2	9.1	88	3 ^b
Dibromotetrafluoroethane	CF ₂ BrCF ₂ Br	2402	10.5	107	2	10.6	74	2.3	19.8 ^b
Dichlorodifluoromethane	CF ₂ Cl ₂	122	10.8	104	3	12	68	4.1	(27) ^c	(74) ^c	...
Methyl bromide	CH ₃ Br	1001	11.3	100	3.4	8.0	100	2.1	80	5	100
Ethyl bromide	C ₂ H ₅ Br	2001	11.7	96	2.8	(24) ^d	(5.5) ^d
Methyl iodide	CH ₃ I	10001	11.7	96	2.8
Chlorobromomethane	CH ₂ ClBr	1011	12.7	80	2.7
Carbon tetrachloride	CCl ₄	104	(15) ^d	(75) ^d	(3) ^d	11.4	68	2.0	3 ^b
Perfluoromethylcyclohexane	C ₆ F ₁₁ CH ₃	CH (M)	(24) ^e	(55) ^e	(7) ^f	3 ^b
Bromochlorodifluoromethane	CF ₂ ClBr	1211	10.7	75	2.3
Dibromodifluoromethane	CF ₂ BrCF ₂ Br	2202	12	66	2.2

(a) Agents were discharged from a 24-12 CO₂ extinguisher charged with 2 lb of agent, and then pressurized with nitrogen at 70 psig. CO₂ discharge pressure in all cases was approximately 800 psig.

(b) Methyl bromide taken as 100%.

(c) Five tests.

(d) Average values for successful extinguishments only. (6 failures in 10 tests.)

(e) See (d), above, (5 failures in 5 tests).

(f) See (d), above, (2 failures in 2 tests).

(g) Not effective in combating the fires.

12. Low Temperature Tests at ERDL. A series of tests designed to duplicate as nearly as possible arctic environment, was undertaken in the ERDL Cold Chamber at temperatures ranging from -55 to -65 F to determine if the otherwise qualified agents were suitable for use under arctic conditions.

To conduct the tests a special assembly was designed, and was constructed in the ERDL Shops. The assembly was semi-automatically and remotely controlled, the actuation of the extinguisher being mechanical, so that the human element in the extinguishment of the test fires was eliminated. The description of the apparatus and the test procedures are contained in Appendix D, Exhibit 10.

During the actual fires the exhaust fan and the precooler system of the cold chamber were operated to insure adequate ventilation of the Chamber. However, the admission of large quantities of air, not completely chilled to -65 F, at essentially 100 percent humidity caused icing in the primary cooling coils of the chamber, which in turn made it impossible to maintain -65 F, without long intervals between tests, therefore, a temperature ranging from -55 to -65 F was maintained.

A summary of the test data is presented in Table XII. In this table the average weights and times required for extinguishing the pan fires with the respective agents are reported. These averages do not include tests in which no extinguishment occurred, or in which definite malfunctioning of the test apparatus was noted. Comparison of the number of valid tests with the number of extinguishments for each agent provides an indication of the reliability of the agents.

III. DISCUSSION

13. General. The initial goals of the laboratory study were to obtain and evaluate a substantial number of compounds, to determine the best of the group with respect to fire suppression, and to determine whether the data on the entire group could be correlated on some basis that would indicate the type of compound that could be expected to possess superior fire inhibiting properties. These goals have been largely accomplished. At present, laboratory work is primarily concerned with establishing the mechanisms responsible for the flame suppressing activity of halogenated agents. The information sought in this study is believed to be the key to the currently unexplained results.

In addition to the study of the extinguishment mechanism (which includes the correlation of physical properties and constants, and the determination of thermal decomposition products with and without fuels and oxygen present), additional tests of compounds

Table XII. Summary of Results of Low Temperature Tests

Agent	Nalon No.	Avg. Ext. Time (Sec)	Avg. Wt. Agent to Ext. (Oz)	No. Valid Tests	No. Ext.	Temp. Range (Deg. F)
<u>Mist Application (400 psig)^a</u>						
Methyl bromide	1001	7.6	33.5	12	6	-56 to -64
Dibromodifluoro-methane	1202	6.6	24.5	11	11	-55 to -65
Bromotrifluoro-methane	1301	3.0	21.0	16	14	-50 to -60
Dibromotetra-fluoroethane	2402	5.5	24.0	10	3	-51 to -58
<u>Straight Stream Application (200 psig)^a</u>						
Methyl bromide ^b	1001	3.5	27.0	3	1	-56 to -57
Dibromodifluoro-methane ^b	1202	4.0	26.0	1	1	-59 to -60
Dibromotetra-fluoroethane ^b	2402	3.0	22.5	1	1	-54 to -55

(a) Extinguisher cylinders were pressurized to the indicated pressure at 70 F with N₂.

(b) Agents naturally liquid at room temperature; commercial carbon tetrachloride nozzle used for application.

containing elements other than carbon, hydrogen and the halogens will be made to verify some of the tentative conclusions. At the termination of these laboratory studies, sufficient knowledge should be attained so that any trial and error investigation of halogenated or vaporizing type extinguishing agents will be unnecessary.

The theoretical significance of the laboratory data and its relation to the selection of an agent for service test are discussed in subsequent paragraphs.

14. Correlation and Analysis of Laboratory Extinguishment Data.
A study of the results of the Purdue and ERDL investigations, and their correlation with those obtained elsewhere, reveals that certain

extinguishing agents are more effective than others under all conditions tested.

a. Correlation of Data. The laboratory n-heptane fire tests were run in the Materials Branch to determine the relative effectiveness of selected agents which had been tested at Purdue. The plot of data in Fig. 2, a comparison on the basis of weight, indicates that a direct relationship exists between the two sets of data. Thus, it appears that the flame inhibiting effect of an agent is a measure of its general fire fighting effectiveness.

As a further check on the results of the flame extinction and inhibition tests on fire fighting agents, a comparison, on the weight basis, was made with test data from outside sources. These include tests performed by the CAA Experiment Station, the Minnesota Mining and Manufacturing Company, and by two British agencies. The data from these sources are contained in Appendix E, Exhibits 1 through 3, respectively, and are summarized in Table XIII, from which it can be seen that while methyl iodide does not perform as well in some actual tests as predicted, the relationship between methyl bromide and carbon tetrachloride is fairly consistent regardless of the source of data.

Table XIII. Comparison of Extinguishment
Data from Various Sources

Agent	Halon No.	% Effectiveness on Weight Basis ^a				
		Pyrene Co., Ltd.	Burgoyne and Richardson ^d	CAA	PRF	MM&M
Methyl bromide	1001	100	100	100	100	...
Methyl iodide	10001	68	...	67	106	95
Carbon tetra- chloride	104	58	47	42	52	57
Carbon dioxide	53.5	17 ^b	71	71 ^c

- (a) Methyl bromide set at 100%
- (b) See Appendix E, Exhibit 1
- (c) See Appendix E, Exhibit 2
- (d) See Appendix E, Exhibit 3

b. Binary Mixtures. In the investigation of binary mixtures, it was originally assumed that the resulting flammability peak could be determined by adding the mole fraction times the flammability peak of the first agent to the product of the same properties of the second agent. However, the validity of this assumption was not borne out by a comparison of the observed results with those calculated (see Table XIV). In this respect it is interesting to apply the LeChatelier reciprocal molar additivity rule⁴ for predicting the lower flammable limits of mixtures of two combustibles. If such a relationship is applied to the data of Table V, the following formula may be used:

$$P_m = \frac{2}{\frac{1}{P_a} + \frac{1}{P_b}},$$

where:

P_m = calculated flammability peak of the equivolume mixture by the above method,

P_a = the flammability peak of component A,

P_b = the flammability peak of component B.

If a direct relationship is assumed, the following equation is used as indicated in Table V:

$$P_c = \frac{P_a + P_b}{2}$$

where:

P_c = calculated flammability peak in the above equation,

P_a and P_b are as indicated previously.

4. The rule is given by H. LeChatelier (Estimation of Fire Damp by Flammability Limits, Ann. Mines, Vol. 19, Ser. 8, (1891) pp. 388-395), and may be written:

$$L_m = \frac{1}{\frac{F_a}{L_a} + \frac{F_b}{L_b}}$$

where:

L_m = lower limit of flammability of a mixture in volume percent,

L_a = lower limit of flammability of component A in volume percent,

L_b = lower limit of flammability of component B in volume percent,

F_a = mole fraction of component A in the fuels, and

F_b = mole fraction of component B in the fuels.

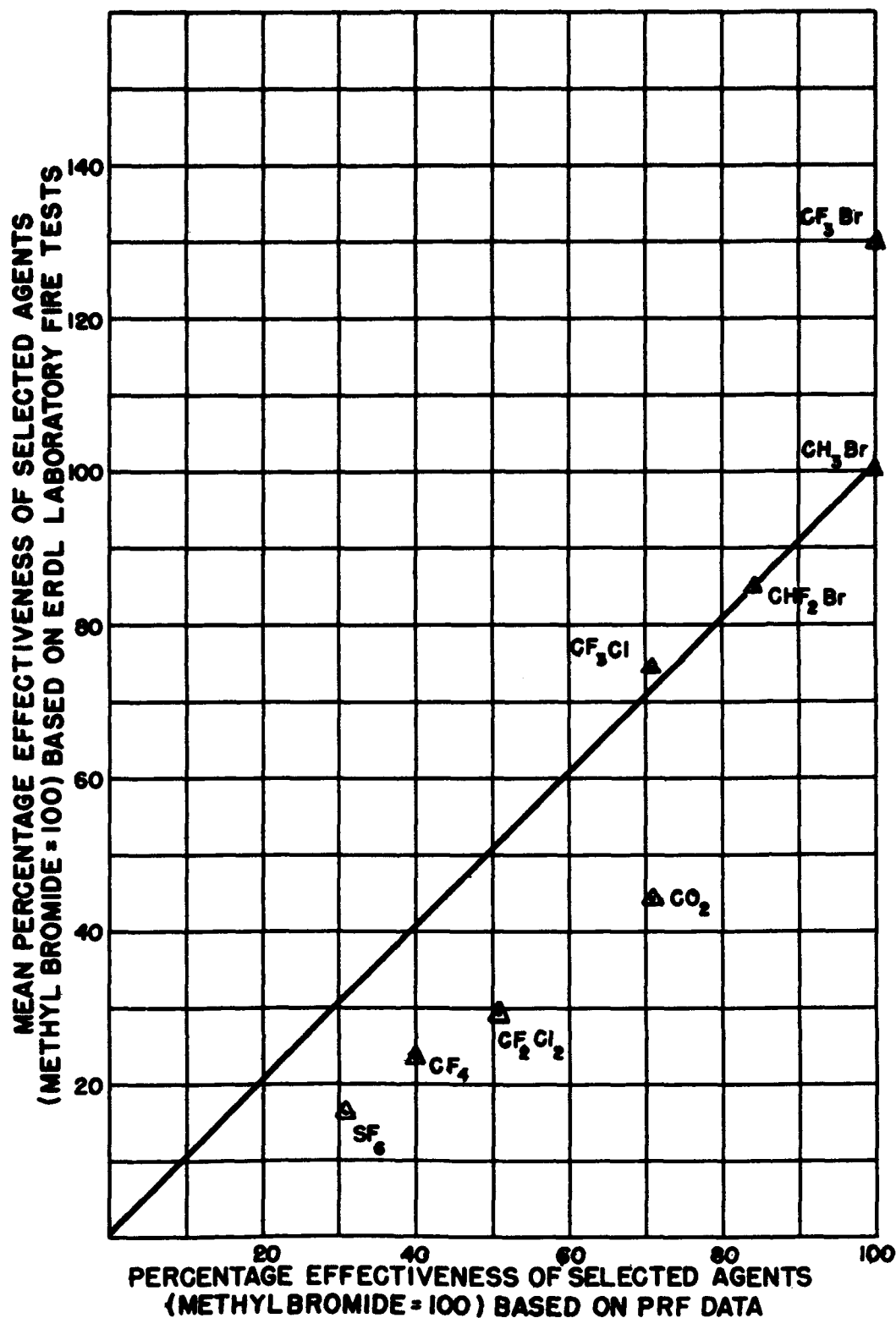


Fig. 2. Correlation of flame inhibition and flame extinguishment data (see Tables III and IV).

The two methods of calculating mean flammability peaks of mixture are compared in Table XIV, below:

Table XIV. Percentage of Agents at Flammability Peaks for Binary Mixtures of Dibromomethane and Selected Agents^a

Agent	Balon No.	Concentration of Agent at Flammability Peak (% by Vol.)				Effect
		P_b	$P_o(b)$	P_o	P_m	
Tribromofluoromethane	1103	4.3	5.3	4.8	4.7	antiennergistic
Perfluoroethylcyclohexane	HP(E)	6.8	5.4	6.0	5.9	synergistic
Ethyl bromide	2001	6.2	5.7	5.7	5.7	asynergistic
Carbon tetrachloride	104	11.5	7.2	8.4	7.2	?
Chloroform	103	17.5	9.3	11.4	8.0	?

- (a) The dibromomethane and selected agents were in each case an equivalent mixture. (Flammability peak of dibromomethane = 5.2%)
 (b) P_o = experimentally observed flammability peak for the mixture.

Although the reciprocal molar additivity rule appears to conform to these data better than the direct molar average values (P_m vs P_o), the small number of instances do not definitely indicate the superiority of either method.

Since the tests revealed no significant increase in effectiveness as a result of the use of a binary mixture, and in view of the limitations of the project, no further work has been undertaken on the subject of mixtures.

c. Use of Various Fuels. Tests of selected agents in inhibiting flames in various fuels indicated that their relative effectiveness did not vary appreciably with a variation of the fuel. However, some correlation was noted between the heat of combustion of the fuel and the mean of the flammability peaks of the agents calculated by the reciprocal method. That is,

$$FP_m = \frac{n}{\frac{1}{FP_a} + \frac{1}{FP_b} + \dots + \frac{1}{FP_n}},$$

n being the number of reciprocal flammability peaks in the summation. Fig. 3 indicates that in most cases the highest flammability peaks are obtained with fuels having high heats of combustion, these being present in a homogenous vapor mixture of fuel, air, and agent. However, in the practical fire fighting tests of Burgoyne and Richardson (see Appendix E, Exhibit 3), it was found that when combustion was supported by the vaporizing fuel, a higher concentration of agent was required to extinguish ethanol fires than was required to extinguish benzene fires. Thus, it appears that factors other than the heat of combustion must be considered in comparing the data from these two sources. Among these are the volatility of the combustible and its rate of diffusion.

d. Variation in Temperature. It is seen from Table VIII that the order of effectiveness of the halogen compounds tested are the same for the range of temperatures studied, i.e., -78 C to -145 C (-108 F to -293 F). This fact is of practical importance, but the irregularities of the flammable areas for the reduced temperatures (see Appendix D, Exhibit 4) have no apparent explanation at present. As more is learned about the flame extinguishing mechanisms of the various agents, further analysis of these data will be undertaken.

e. Effect of Combustion Tube. The results of the flammability determination with methyl bromide, indicating a lower flammability peak in copper vessels, are with precedent, since in experiments with mixtures of hydrogen and oxygen in silver vessels the reaction rate of the gases was significantly retarded.⁵ It was hypothesized that the presence of silver in vapor form interfered with flame propagation by blocking hydrogen radicals. The presence of silver vapor was attributed to the action of hydrogen radicals at the vessel surface. It seems possible that the same mechanism could act in a copper vessel. The PRF has made no further experimental investigations of this phenomenon since it would have entailed the use of additional and diversified equipment, whereas other investigations were more pertinent to the immediate problem of explaining the mechanisms of the individual agents.

15. Effect of Molecular Structure on Extinguishment. In this theoretical analysis of data, certain correlations are apparent when the reciprocals of the flammability peaks are examined or manipulated. This appears logical, since the agent blocks or inhibits flame propagation which would otherwise occur. The reciprocal of the flammability peak is a direct function of the ability of an agent to inhibit a flame, whereas the flammability peak is an inverse function of the same action. By considering the flammability peaks of the various agent-fuel mixtures as the

5. B. Lewis and G. VonElbe, Combustion, Flames and Explosions of Gases, (Cambridge: Cambridge University Press, 1938).

measure of flame "conductivity" and the reciprocals of the flammability peaks as a measure of flame "resistivity" the following approximate atomic resistivities were deduced after several trial and error calculations.⁶

Fluorine	1
Chlorine	2
Bromine	10
Iodine	16

From these atomic resistivities the flammability peak of the various halocarbons may be estimated by means of the following formula:

$$FP_a = \frac{100}{\Sigma R_a}$$

where:

$$\Sigma R_a = AR_f + BR_c + CR_b + DR_i = \text{molar resistivity,}$$

R_f , R_c , R_b and R_i being the atomic resistivity, and A, B, C, and D being the number of fluorine, chlorine, bromine, or iodine atoms in the respective agents. These resistivities are approximate, since any more exact determination would have been more laborious than warranted until the full significance of these data is ascertained.⁷

6. The Purdue data were examined to determine if the flammability peaks could be correlated in any way with the chemical structure. In one investigation the reciprocals of the flammability peaks were calculated. On examination of the reciprocals, an apparent additive effect of the various halogens of the halocarbons was noted. The term resistivity is used to indicate a measure of the resistance to flame propagation.

7. It is of further interest to note that the atomic resistivity rule is of the same form as the LeChatelier rule (see par. 14), i.e., if $FP_a = \frac{100}{AR_a + BR_b}$, etc. then a "reciprocal conductivity" can be used in place of the resistivity so that: $FP_a = \frac{100}{\frac{A}{C_a} + \frac{B}{C_b}}$,

which is of the same form as

$$\frac{\frac{F_a}{P_a}}{1} + \frac{\frac{F_b}{P_b}}{1}$$

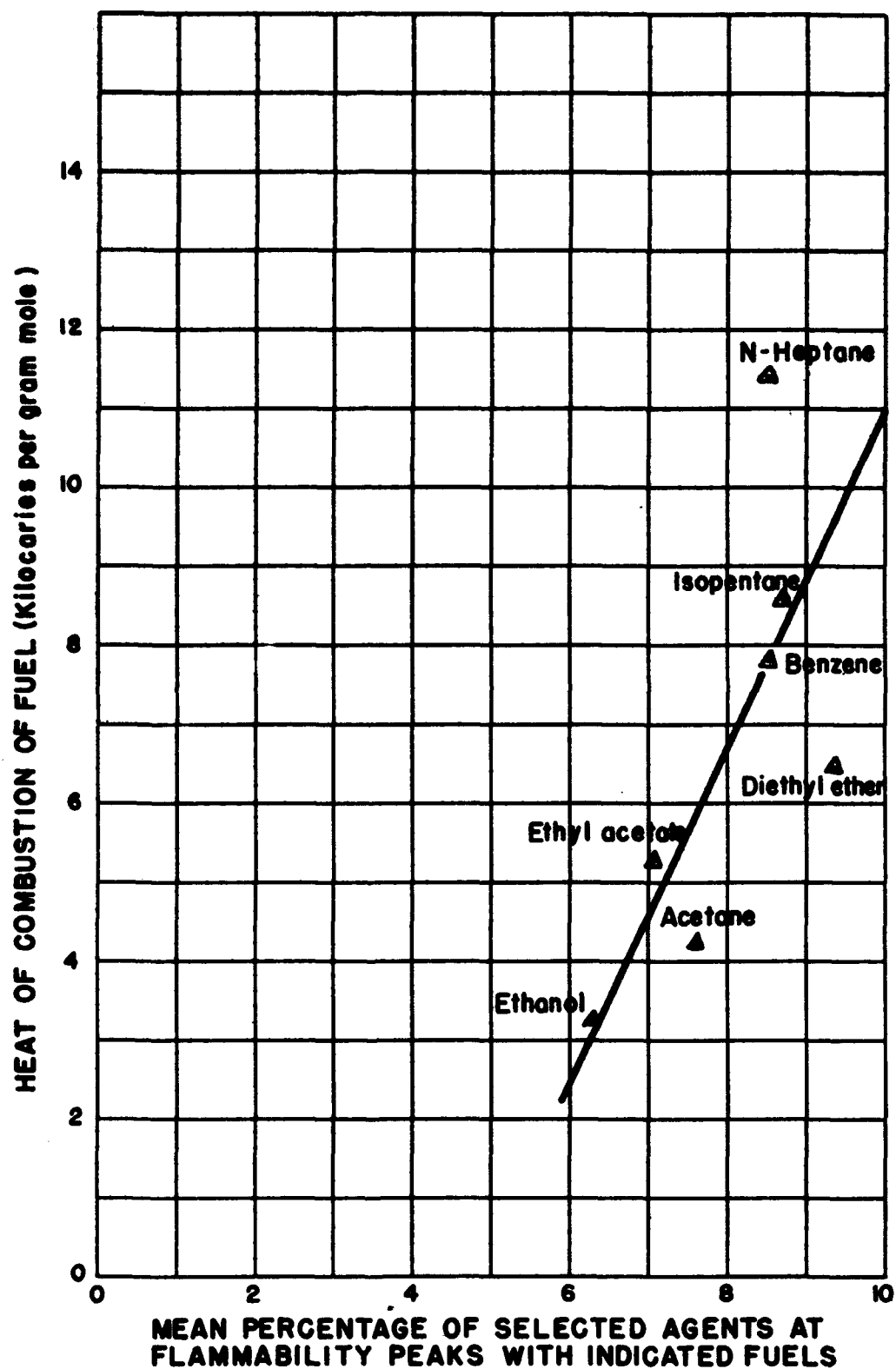


Fig. 3. Relation of Heat of combustion to flammability peak.

Most of the flammability peaks thus obtained as can be seen from Table XV, correspond to the observed values. Where large deviations occur, it is possible that they are the result of variations in the mechanisms of extinguishment. There is also an indication that non-symmetrical compounds deviate in a positive manner (i.e., better than predicted by atomic resistivities) from the approximated performance in inhibiting flame propagation. Calculated and observed flammability peaks are cited particularly for the following:

<u>Agent</u>	<u>Halon No.</u>
2-bromo-1,1,1-trifluoropropane	3301B
3-bromo-1,1,1-trifluoropropane	3301C
Bromotrifluoromethane	1301
1-bromo-2,2-difluoropropane	3201
2-bromo-1-chloro-1,1-difluoropropane	3211B
2-bromo-1,1,1-trifluoroethane	2301

The weight effectiveness of a halogenated agent may also be estimated, on the basis of methyl bromide as 100 percent, as being

$$E_w = \frac{950 \Sigma R_a}{M}$$

where:

ΣR_a is as above

M = molecular weight of the agent

$$950 = 100 \times \left(\frac{\text{molecular weight of methyl bromide}}{R_b} \right)$$

This estimated effectiveness corresponds in the instances where the calculated and observed flammability peaks are in agreement.

Thus, the estimated effectiveness of trichloromethane (chloroform) is

$$\frac{950 \times 6}{119.5} = 48 \text{ percent (observed = 44 percent),}$$

and that of carbon tetrachloride is

$$\frac{950 \times 8}{154} = 49 \text{ percent (observed = 52 percent).}$$

Table XV. Flammability Resistivity Analysis of Purdue Data

Agent (1)	Calon No. (2)	Molar Resis- tivity (R_v) (3)	Reciprocal of Observed Flammability Peak $\times 100$ ($\frac{100}{FP_o}$) (4)	Calculated Flammabil- ity Peak (FP_a) (5)	Observed Flammabil- ity Peak (FP_o) (6)
Dibromodifluoromethane	1202	22	23.8	4.5	4.2
1,2-dibromo-1,1-difluoroethane	2202A	22	23.3	4.3	4.3
Tri bromofluoromethane	1103	31	23.2	3.2	4.3
1,2-dibromo-2-chlorotrifluoroethane	2312	25	22.6	4.0	4.6
2-bromo-1,1,1-trifluoropropane	3301B	13	20.4	7.7	4.9
1,2-dibromotetrafluoroethane	2402	24	20.4	4.2	4.9
1,2-diiodotetrafluoroethane	24002	36	20.0	2.8	5.0
Dibromomethane	1002	20	19.2	5.0	5.2
Iodopentafluoroethane	25001	21	19	4.8	5.3
3-bromo-1,1,1-trifluoropropane	3301A	13	18.5	7.7	5.4
Ethyl iodide	20001	16	17.8	6.2	5.6
Bromopentafluoroethane	2501	15	16.3	6.6	6.1
Methyl iodide	10001	16	16.3	6.2	6.1
Bromotrifluoromethane	1301	13	16.3	7.7	6.1
Ethyl bromide	2001	10	16.2	10	6.2
1-bromo-2,2-difluoropropane	3201D	12	15.9	8.3	6.3
2-bromo-1-chloro-1,1-difluoropropane	3211B	14	15.6	7.1	6.4
Dibromofluoromethane	1102	21	15.6	4.8	6.4
2-bromo-1,1,1-trifluoroethane	2301	13	14.7	7.7	6.8
Perfluoro(ethylcyclohexane)	MP(E)	16	14.7	6.2	6.8
Perfluoro(1,3-dimethylcyclohexane)	MP(M)	16	14.7	6.2	6.8
Perfluoro(1,4-dimethylcyclohexane)	MP(M)	16	14.7	6.2	6.8
Iodotrifluoromethane	13001	19	14.7	5.3	6.8
1-bromo-2-chloroethane	2011B	12	13.9	8.3	7.2
2-bromo-1-chloro-1,1-difluoroethane	2211	14	13.3	7.1	7.2
Perfluoro(methylcyclohexane)	GM(M)	14	13.3	7.1	7.5
Perfluoroheptane	GP	16	13.3	6.2	7.5
Chlorobromomethane	1011	12	13.1	8.3	7.6
Bromodifluoromethane	1201	12	11.9	8.3	8.4
1,2,2-trichlorotrifluoroethane	233	9	11.1	11.1	9.0
Hydrogen bromide	...	10	10.7	10	9.3
Bromochlorodifluoromethane	1211	14	10.7	7.2	9.3
Methyl bromide	1001	10	10.3	10	9.7
Difluorovinyl bromide	...	12	10.3	8.3	9.7
Perfluorobutane	DJ	10	10.2	10	9.8
Silicon tetrachloride	...	8	10.1	12.5	9.9
1,2-dichlorotetrafluoroethane	242	8	9.4	12.5	10.8
Carbon tetrachloride	104	8	8.7	12.5	11.5
2-chloro-1,1,1-trifluoropropane	331B	5	8.3	20	12.0
3-chloro-1,1,1-trifluoropropane	331A	5	8.2	20	12.2
Chlorotrifluoromethane	131	5	8.1	20	12.3
Hexafluoroethane	26	6	7.5	16.8	13.4
Dichlorodifluoromethane	122	6	6.7	16.8	14.9
Chloroform	103	6	5.7	18.8	17.5
Fluoroform	13	3	5.6	33.3	17.8
Chlorodifluoromethane	121	4	5.6	25	17.9
Octafluorocyclobutane	48(c)	8	5.5	12.5	18.1
Sulfur hexafluoride	...	6	4.9	16.8	20.5
Boron trifluoride	...	3	5.0	33	20.5
Phosphorus trichloride	...	6	4.5	16.7	22.5
Hydrogen chloride	...	2	3.9	50	25.5
Carbon tetrafluoride	14	4	3.8	25	26

Although at present no definite explanation can be made of the theoretical significance of the atomic resistivities, Table XVI offers a possible lead for further correlation of the flame extinguishing properties of the various halogens when additional basic physical data are available.

The specific resistivities shown in Table XVI indicate that there is no practical advantage in iodine over bromine, on the direct weight basis as a component of a fire extinguishing agent.

Table XVI. Physical Characteristics of Halogens

Characteristic	Fluorine	Chlorine	Bromine	Iodine
Atomic weight	19	35.5	80	127
Atomic resistivity	1	2	10	16
Specific resistivity	0.059 ^a	0.057 ^a	0.125 ^a	0.126 ^a
Atomic number	9	17	35	53
Atomic number ratio	1 ^b	1.9 ^b	1 ^c	1.5 ^c
Electrons in shells	2,7	2,8,7	2,8,18,7	2,8,18,18,7
Boil point liquid(K)	86 ^d	239 ^d	332 ^d	456 ^d
Liquid density at B.P. (gm-cm ⁻³)	1.11 ^d	1.557 ^d	2.98 ^d	4.0 ^d
(Liquid density at B.P.) ² (gm ² -cm ⁻⁶)	1.21	2.42	8.9	16

(a) Specific resistivity = $\frac{\text{atomic resistivity}}{\text{atomic weight}}$

(b) Ratio based on atomic number of fluorine

(c) Ratio based on atomic number of bromine

(d) International Critical Tables, McGraw Hill (1926)

16. Effects of Application Rate, Molecular Weight, and Temperature on Extinguishment. While the practical fire tests in general confirmed the results obtained in the laboratory, certain differences appeared to result from the rate of application and the molecular weight (vapor density) of the agent.

The discharge rate is, at a given application pressure, a function both of the relative volatility and of the molecular weight.

It was noted that the effectiveness of both methyl bromide and dibromodifluoromethane increased with a reduction of charge pressure from 800 to 400 psig. This effect is similar to that noted in the comparison of the Civil Aeronautics Authority data with those of the PRF (Appendix E, Exhibit 1). These tests and the evaluation of various orifice sizes with dibromodifluoromethane (see Appendix D, Exhibit 9) suggests that the optimum application rate for a given type of fire varies with the particular agent. Also, dibromodifluoromethane was most effective on the Class B 2-foot tub fire, whereas bromotrifluoromethane was most effective on the Class C fire. This suggests that the optimum application rate may also vary from one type of fire to another.

Since the bromofluorocarbons used were produced on a laboratory scale, there was not a sufficient quantity available for the extensive program required for a comprehensive study of the optimum discharge rate for the finally selected agent. This study will be conducted as soon as the agent becomes available on a commercial basis. With respect to the influence of molecular weight on the performance of an agent in actual fire tests, it is possible to propose two hypotheses: (1) a compound of molecular weight several times that of air should persist in the area of application longer than would a compound of essentially the same density as air (such as CO₂), thus tending to prevent flashbacks; (2) a less dense compound will be able to displace more air from a burning surface per unit weight applied, and it will diffuse more rapidly into the flame front. However, it appears from the limited tests that molecular weight of the halogenated agents is of less importance than the rate of application.

The Cold Chamber tests indicate that the application of dibromodifluoromethane either as a mist or as a straight stream from containers pressurized with nitrogen is both effective and practical. They also indicate that the relative effectiveness of the agents applied as a mist was as predicted by laboratory studies⁸, except that bromotrifluoromethane, which is a gas at -65 F, is more effective than dibromodifluoromethane.

A comparison of methods of application under low temperature conditions (mist vs straight stream) and the relative effectiveness of the agents applied as straight streams is not possible on the basis of the limited data obtained (only 4 tests of straight stream application were made). It should be noted, however, that the mist application caused only a slight fuel dilution, whereas in the straight stream application the burning fuel was diluted critically, thus effecting extinguishment (see Appendix D, Exhibit 10).

8. Less dibromotetrafluoromethane than dibromodifluoromethane (by weight) was used in the extinguishments effected, but the former failed in 7 out of 10 attempts.

17. Physical and Chemical Characteristics of Agents. In addition to establishing the extinguishment characteristics of the various agents under test, it was also necessary to determine their toxicity, their corrosiveness, and their electrical conductivity.

a. Toxicity. The toxicity data on the pyrolyzed vapors of chlorobromomethane, dibromodifluoromethane, and 1,2-dibromotetrafluoroethane cannot be used to demonstrate that any one of these compounds is more or less toxic than the other, but it does indicate that the three agents have toxicities of the same order of magnitude. (In the relative values of toxicities reported by the approximate method, significant differences are indicated only when the toxic concentration differ by factors of 2 or more.) The relative toxicities indicated by the series of 15-minute exposures to the natural vapors of the agents are essentially the same as those that would be indicated by a series of 5- or 10-minute exposures to the same agents. This is true because the mechanisms of toxicity are the same for exposure periods ranging approximately from 5 minutes to 1 hour.

The pyrolysis test used was selected to give an expedient indication of toxic products which might be formed when applying the various agents to a fire. Since the vapors were pyrolyzed in a completely oxidizing atmosphere the test may be more severe than the conditions expected in most small fires. In the final evaluation projected for bromotrifluoromethane and dibromodifluoromethane the toxic effect of the agents when applied to actual fires will be determined.

The most striking anomaly noted in the data collected by the Chemical Center is the great reduction in the toxicity of the methyl bromide vapors when pyrolyzed. This has been explained as resulting from the conversion of the methyl bromide to carbon dioxide and hydrogen bromide, both of which are considerably less toxic than the original methyl bromide.

In the screening data it was shown that either bromotrifluoromethane or dibromodifluoromethane will meet the military requirements concerning toxicity. The greater toxicity of the pyrolysis products of dibromodifluoromethane over those of methyl bromide is not a critical factor because in actual fires the toxicity of carbon monoxide and other combustion products will in most cases be greater than that of the pyrolysis products of the agent. However, distinct advantage is seen in bromotrifluoromethane over dibromodifluoromethane insofar as natural vapor and pyrolyzed vapor toxicities are concerned.

It is seen that the more completely fluorinated the halocarbon, the lower is its toxicity, as a general rule.

b. Corrosion. As a class of compounds, the fluorocarbons were the least corrosive (most stable) of the compounds investigated and the monohaloalkanes the most corrosive (least stable), while the halohydrocarbons containing halogen atoms on adjacent carbon atoms were less stable than those containing halogen atoms in the 1-3 position. This is illustrated by the fact that 2-bromo-1,1,1-trifluoropropane was less stable than 3-bromo-1,1,1-trifluoropropane. This type of instability is to be expected, since dehalogenation, one of the expected reactions between a metal and a halohydrocarbon, occurs more readily when the halogen atoms are on adjacent carbon atoms than when there is a carbon atom between the two carbon atoms holding the halogen atoms.

That the halogen compounds proved to be less corrosive to the metals at 200 F than at 392 F was also to be expected, since, in general, the rate of a reaction doubles each time the temperature is increased by 18 degrees F. Specifically, for bromotrifluoromethane no measurable corrosive action was noted at 392 F, and it seems probable that any compound shown to be reasonable non-corrosive at 392 F or 200 F will meet the requirements for a fire extinguishing fluid.

Since there have been no unexpected deviations in the stability of the halogen-containing compounds, this phase of the work was temporarily discontinued. At present further corrosion tests are underway with bromotrifluoromethane and dibromodifluoromethane.

c. Electrical Conductivity. Certain fluorocarbons have been found to be non-conductors of electricity. Although it is believed that the bromofluorocarbons, which have essentially the same structure, will also be non-conductive, the most effective of these latter agents are currently being tested to determine their electrical resistivity.

18. Findings. The following technical findings are indicated by the laboratory and engineering fire tests of the agents under study:

a. The flame inhibition method is a convenient means for predicting the fire extinguishing characteristics of a vaporizing agent.

b. The indicated correlation of flame inhibiting properties of the agents with their chemical structures suggests the existence of a theoretical explanation for the mechanisms by which they extinguish fires.

c. The halocarbons and halohydrocarbons of one or more bromine atoms per carbon atom exhibit greater flame inhibiting effectiveness on a weight basis than do the corresponding chlorides and fluorides, while the corresponding iodides are no more than equal to the bromides in this respect.

d. Binary mixtures of the agents tested exhibit no significant increase in flame inhibiting effectiveness over that of the individual agents concerned.

e. The flame inhibiting effectiveness of binary mixtures (or multicomponent mixtures) can be roughly approximated but not precisely predicted from the performance of the individual components.

f. The relative flame inhibiting effectiveness of any of the agents investigated does not vary appreciably with variations in the type of fuel (hydrocarbon or oxyhydrocarbon), or of the temperature of the atmosphere in which the flame is propagated.

g. In halocarbons of similar structure the greater the relative number of fluorine atoms in the molecule, the less toxic it will be.

19. Selection of an Agent for Service Test. Both the laboratory and the engineering test data (including the reduced temperature tests) show that two compounds, bromotrifluoromethane and dibromodifluoromethane, have been consistently more effective than methyl bromide in extinguishing fires. Of the two agents under consideration, dibromodifluoromethane was found to be the more effective by a narrow margin at room temperature, all of the studies taken as a whole, whereas bromotrifluoromethane was the more effective at -60 F.

The corrosive effects of bromotrifluoromethane appears to be practically negligible for the common metals. In tests now in progress at the ERDL, or to be undertaken, the effect of this agent, and of dibromodifluoromethane, both on metals and on other materials, is being determined.

With respect to the toxicity of these two agents, the tests with rats show bromotrifluoromethane to be 1/28 and dibromodifluoromethane to be 1/2 as toxic as carbon tetrachloride (methyl bromide is 5 times as toxic as carbon tetrachloride). The large relative difference in toxicity is taken as clear evidence of the superiority of bromotrifluoromethane over dibromodifluoromethane in this respect. The effect of these agents on humans has not been determined, but the results on rats indicate that bromotrifluoromethane may be used with relative safety in an inclosed area such as the interior of a vehicle, tank, or plane. An approximation of the safety factors of these agents in relation to that of carbon tetrachloride or methyl

bromide, if 3 pounds (weight of agent in current CTC hand extinguishers) were released in a space having an interior volume of 200 cubic feet (approximately that of a combat tank), would be as follows:

<u>Agent</u>	<u>Tank Vapor Conc. (ppm)</u>	<u>Relative Safety Factor⁹</u>
Bromotrifluoromethane	35,000	24
Carbon dioxide	125,000	5.3
Dibromodifluoromethane	26,000	2.1
Carbon tetrachloride	30,000	1.0
Methyl bromide	58,000	0.1

Such a range of safety factors is interpreted as indicating that the effect on a human being of a 15-minute exposure to the various agents, under the conditions given, would conceivably range from slight or none for bromotrifluoromethane to probably lethal for methyl bromide. Another factor in toxicity, of course, is the effect of pyrolysis products that are themselves toxic. Here, again, bromotrifluoromethane has shown its superiority over dibromodifluoromethane in the tests thus far completed.

No known practical extinguishing agent is self-expelling over the expected range of storage and use (-65 to +160 F). Both of the agents under consideration can be applied from cylinders pressurized with inert gas, neither being suitable for use in pump type extinguishers such as those currently used for carbon tetrachloride. When applied from a pressurized container (400 psig at 70 F) the discharge ranges from a fine mist at low temperatures to a gas at the upper limit, bromotrifluoromethane being the more volatile of the two. At room temperatures and below, dibromodifluoromethane can also be applied as a solid stream, using a lower discharging pressure (under 200 psig at 70 F). However, neither agent solidifies on discharge at -65 F, as will carbon dioxide.

These agents require the same production facilities as the fluorinated refrigerants (freon), and for this reason their cost will be comparable. For this same reason, neither agent possesses an appreciable inherent advantage over others with respect to cost. Although their cost will be considerably higher than that of agents now in use (carbon tetrachloride is currently quoted at 8¢ per lb), it should be noted, that the more expensive

9. Relative safety factor = $\frac{\text{Tank vapor concentration (ppm)}}{\text{Approximate lethal concentration (ppm)}}$

fluorinated refrigerants were accepted in place of those previously used because of their low toxicity. A similar preference is anticipated for bromotrifluoromethane.

The compliance of the selected agents to the military characteristics is shown in Table XVII. It is noted that both bromotrifluoromethane and dibromodifluoromethane comply with the military characteristics, which are somewhat general in nature. For this reason, the governing factor in the final selection of one of these agents for service test is that of toxicity, their fire fighting effectiveness and other characteristics being approximately equal.

The service test of a bromofluorocarbon agent has been approved by the CETC¹⁰, and bromotrifluoromethane has been selected as the specific agent to be thus tested, with delivery for this purpose anticipated for the spring 1951.

20. Future Work. While the service tests of bromotrifluoromethane are in progress, work will continue on the following phases of the present investigation:

a. Completion of toxicity investigations. (More comprehensive toxicological data will be required before clearance of the new agent can be obtained from the Surgeon General.)

b. Completion of corrosion and mechanism and pyrolysis product studies, and development of theoretical correlations.

c. Completion of the design for the new extinguisher. (Preliminary requirements have been set up, and two contracts have been negotiated with industry to produce expendable extinguisher units for use in service testing the agent.)

d. Engineering testing and studying of horn and extinguisher orifice design to provide optimum performance of the new agent in the new extinguisher. (This study is projected for execution as soon as the new agent is available in larger quantities.)

IV. CONCLUSIONS

21. Conclusions. It is concluded that:

a. Of all the agents tested, bromotrifluoromethane best suits the actual military requirements for a fire extinguishing agent, and is superior to methyl bromide and carbon tetrachloride.

10. CETC Meeting 205, Item 1083, 16 November 1949.

Table XVII. Compliance to Military Characteristics and Comparison with Standard Commercial Agents.

Military Characteristics	Methyl Bromide	Carbon Tetrachloride	Carbon Dioxide	Chlorobromo-methane	Bromo-trifluoro-methane	Dibromodifluoro-methane	Basis of Comparison
The agent shall be suitable for use in combating Class B and C fires	Approximately twice as effective as carbon tetrachloride	Comparator	One and one-half times as effective as carbon tetrachloride	Approximately one and three-fifths as effective as carbon tetrachloride	Essentially equal in effectiveness to methyl bromide. Approximately twice as effective as carbon tetrachloride	Essentially equal in effectiveness to methyl bromide. Approximately twice as effective as carbon tetrachloride	Laboratory data (see Table XII)
It shall not be more toxic than carbon tetrachloride	Five times as toxic as carbon tetrachloride	Comparator	One twenty-third as toxic as carbon tetrachloride	Approximately one-half as toxic as carbon tetrachloride	One twenty-eighth as toxic as carbon tetrachloride	One-half as toxic as carbon tetrachloride	Approximate lethal concentration (see Table X)
It shall be suitable for use at temperatures of from +160 F to -65 F	Suitable	Solidifies at -7.6 F. Releases winterization (AW-10-05 450-2)	Not suitable at reduced temperatures	Suitable over entire temperature range	Suitable over entire temperature range. More effective than dibromodifluoro-methane at -65 F	Suitable over entire temperature range	Cold Chamber Tests (see Table XII)
It shall not deteriorate when transported or when stored for periods of time up to five years under any climatic conditions	Stable under storage conditions	Stable under storage conditions	Stable under storage conditions	Stable under storage conditions	Higher stability than methyl bromide or carbon tetrachloride by reason of fluorine content	Higher stability than methyl bromide or carbon tetrachloride by reason of fluorine content	----
It may be produced in quantity within reasonable cost limits, and with existing production facilities	In commercial production	In commercial production	In commercial production	In commercial production	Produced by fluorination processes as used for the production of freon type refrigerants	Produced by fluorination processes as used for the production of freon type refrigerants	----
Its corrosive effects shall not be greater than those of standard carbon tetrachloride fire extinguisher fluid	Non-corrosive to common metals	Slightly corrosive (negligible when inhibited by traces of Cl_2). Most corrosive to aluminum under aqueous conditions	Non-corrosive	Slightly corrosive. Most corrosive to aluminum	Non-corrosive to common metals. No effect on other materials to be investigated	Anticipated to be non-corrosive to common metals. No effect on other materials to be investigated	Laboratory data (see Appendix D, Exhibit 6)
It shall be a non-conductor of electricity	Non-conductor	Non-conductor	Non-conductor	Non-conductor	Non-conductor	Non-conductor	As a class, all these agents non-conductors. Specific data being obtained


(a) Carbon dioxide winterized with nitrogen in accordance with ARPD-05-45-1 is not entirely reliable at low temperatures (around -60 F).

b. As a military fire fighting agent, dibromodifluoromethane is equivalent to bromotrifluoromethane in all respects except that of toxicity.

V. RECOMMENDATION

22. Recommendation. It is recommended that service tests be conducted on bromotrifluoromethane as a fire extinguishing agent for Class B and C fires.

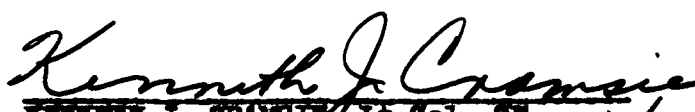
Submitted by:


 J. E. WATSON
 Project Engineer

Forwarded by:


 K. L. TREIBER
 Chief, Petroleum Distribution Branch

Approved 18 August 1950 by:


 KENNETH J. CRANSIE, Lt Col. CE
 Chief, Civil & Military Engineering
 Department

APPENDICES

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APPENDIX AAuthority

SECURITY CLASSIFICATION - UNCLASSIFIED

RESEARCH AND DEVELOPMENT PROJECT CARD (SEE PROJECT NO. 1)		PROJECT NO. 8-76-04-003
1. PROJECT TITLE FIRE EXTINGUISHING AGENT, IMPROVED, SELF-CONTAINED		OLD PROJ. NO. 8-76-04-003
2. BASIC FIELD OR SUBJECT		3. SUB-FIELD OR SUBJECT AND CODE
Fire Fighting		Fire Fighting
4. CONTACT AGENCY Office, Chief of Engineers	10. DISTRIBUTION AND/OR LOCATION Engr. Res. & Dev. Laboratories Perdue Research Foundation	CONTRACT NO. & NO. 44-009ENG507
5. DIRECTING AGENCY Engr. Res. & Dev. Div., MO, OCE	11. PARTICIPATING AGENCY Office, Chief of Engineers	12. VISUAL REFERENCE JULY 48 JULY 48 DEC. 48 DEC. 49 12. VISUAL REFERENCE 48 75 49 10 50
13. PARTICIPATION AND/OR COORDINATION		14. DATE APPROVED 31 January 1947 by WDOS
15. PROJECT NO. 1083, CETC Meeting #169		16. SECURITY 2-1 / 14
17. REQUIREMENT AND/OR JUSTIFICATION There is a requirement for a fire extinguishing agent equal to or superior to methyl bromide in its effectiveness in the extinguishment of fires, and no more toxic than carbon tetrachloride. This development may result in an item of material that possesses such marked superiority over existing items that complete replacement will be justified.		
18. BRIEF OF PROJECT AND OBJECTIVE		
a. REFERENCES: (1) Report of Preliminary Tests of "CB" Fire Extinguishing Agent by Engineer Research and Development Laboratories 14 August 1946.		
b. OBJECTIVE: (1) Development of an improved, self-contained fire extinguishing agent to replace existing agents used in combating flammable liquid and electrical fires.		
c. MILITARY CHARACTERISTICS: (1) The agent shall be suitable for use in combating Class "B" and "C" fires. (2) It shall not be more toxic than carbon tetrachloride. (3) It shall be suitable for use at temperatures from 120 degrees F to at least minus 50 degrees F, and as near to minus 70 degrees F as possible (4) It shall not deteriorate when transported, or when stored for periods of time up to five years, under any climatic conditions. (5) It may be produced in quantity within reasonable cost limits, and with existing production facilities. (6) Its corrosive effects shall not be greater than that of standard carbon tetrachloride fire extinguisher fluid. (7) It shall be a non-conductor of electricity.		
d. DISCUSSION: (1) Preliminary studies of fire extinguisher media have included a study of a new agent captured in Germany which appears to have desirable characteristics as a fire extinguishing agent. This agent has a chemical nomenclature of "monochloromonobromomethane" which, for simplicity, is being called "CB". A limited quantity has been produced and tested. The results of these preliminary tests have		
22. JPRS []	FC	IC & P
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JPRS FORM 12, 1 APR 1947

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d. DISCUSSION (Continued):

- (1) proved encouraging.
- (2) The agencies interested in this project in addition to the Corps of Engineers are the Army Ground Forces, Air Force, and the Navy.

e. PROJECT PLAN:

- (1) Funds will be provided to a qualified research agency to search the chemical compound field for an agent equal or superior to methyl bromide in its effectiveness in extinguishing fires, and which is no more toxic than carbon tetrachloride. Any agents which laboratory tests indicate are worthy of trial will be procured for thorough testing by the Engineer Research and Development Laboratories or other qualified agency. If necessary, an extinguisher for applying the agent will be developed.
- (2) The Perdue Research Foundation is to explore the Flourine field to determine the suitability of oven flourine compounds as fire extinguishing agents.

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PAGE 2 OF 2 PAGES

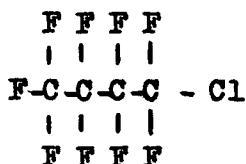
APPENDIX BHalon Nomenclature

To enumerate the halocarbons and halohydrocarbons under study in Project 8-76-04-003, the following nomenclature has been devised.

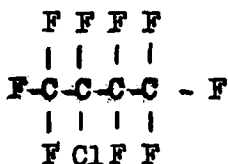
To designate a saturated halocarbon a series of digits are used, the first corresponding to the number of carbon atoms, the second to the number of fluorine atoms, the third to the number of chlorine atoms, the fourth to the number of bromine atoms, and the fifth to the number of iodine atoms in the halocarbon or halohydrocarbon molecule. Hydrogen is not designated, and the final zeros of digits are not written. A cyclic compound is suffixed by (c), or by the following designations of an aliphatic group which is coupled to the ring:

methyl (M)
ethyl (E)
1,2 dimethyl (2M)
1,2,3 trimethyl (2,3M)
1,4 diethyl etc (4E) etc

Isomers are designated by suffixes A,B,C, etc., and if symmetrical are written without suffix. Non-symmetrical compounds are designated by the letters A,B,C, etc., corresponding to the location of the odd halogen atoms. Thus, the compound



is designated halon 491A, and the compound



is designated halon 491B.

In the event that the number of any type of halogen atom in the compound exceeds nine, letters are used in place of numerals. Thus, if thirteen fluorine atoms are present, the letter M is used to designate the number of fluorine atoms.

APPENDIX C

Theory of Fire Extinguishment

1. Nature of Flame. There are several ways of explaining flame propagation. One concept proposes free radical chain reactions, which, in the case of hydrogen burning in oxygen, is explained as follows;¹



In this mechanism the free radicals may be said to form at elevated temperatures, and the radicals diffusing ahead of the flame initiate the reaction in the unburned portion of the gas. Another concept proposes that energy liberated in combustion is radiated to adjacent unburned molecules, thus energizing them sufficiently so that they undergo combustion.

In either case free radicals may provide the reaction mechanism. The difference between the two concepts is in the manner in which energy is transferred from the reacting to the nonreacting zone. This energy is necessary to initiate or sustain combustion. Hydrogen and oxygen may be mixed at room temperature without reaction, but the application of a spark or flame will initiate a reaction that will propagate itself to completion. In mixtures of hydrogen and chlorine, light energy only is needed to initiate the reaction. It must be noted that in order for the reactions to sustain themselves, each molecule must be activated with sufficient energy to react. The resulting net energy change (q) is expressed by the equation

$$q = E_2 - E_1$$

where

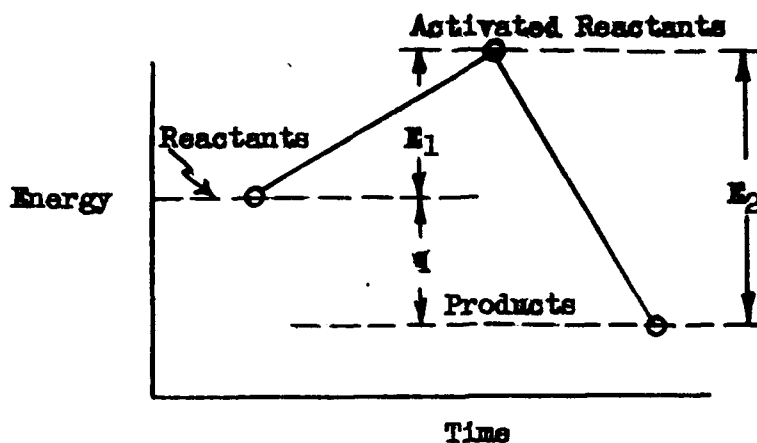
E_1 = activation energy, and

E_2 = energy liberated in reaction.

When q is positive, as shown, the reaction is exothermic, as is the case of a combustion reaction.

¹

B. Lewis and G. Von Elbe Combustion, Flames and Explosions of Gases, (Cambridge: Cambridge University Press, 1938).



2. Mechanism of Extinguishment. If oxygen dilution were the only factor, inert gases would be essentially equivalent in their effect, volume for volume. Hence, a fire extinguishing agent must positively deter flame propagation, as well as effect oxygen dilution in the air. It follows that a fire extinguishing agent may (1) block the free radical chain by reaction, or by absorbing radical energy; (2) it may absorb energy directly in the flame zone, reducing the energy level below the activation energy for the combustion reaction; or (3) it may form metastable compounds or complexes with free radicals, thus preventing their diffusion to unburned gases.

Evidence indicates that the effectiveness of the halocarbon agent varies with the type of halogen present, as indicated in the body of this report, so that in this case the blocking or energy absorbing property appears to be a function of the halogen group.

3. Additional Properties of Agents used in Fire Extinguishing. On further consideration of activation energies, it is seen that any compound, or even atoms, may be decomposed if sufficient energy is expended. The initial energy necessary is the activation energy for the particular reaction. Thus a fire extinguishing agent may be decomposed, no matter how stable it may be. The criterion of this type of reaction is the magnitude of the activation energy.¹ High

¹ In this investigation, an agent which performs satisfactorily in Class B and C fires is sought, and it is not expected that such an agent will be satisfactory, for instance, against magnesium fires, where the energy level is extremely high, and an exothermic reaction is possible between the magnesium and the halogen of the halocarbon.

activation energy indicates difficulty in initiating the reaction, and a slow rate of reaction (Arrhenius equation).

Thus, the decomposition activation energy for the agent must be sufficient to assure that decomposition is at a minimum while the agent is exposed to the flame, and that there is no possibility of the agent reacting directly with combined carbon or hydrogen components of Class B and C fires with the liberation of heat.

Fluorocarbons are quite stable and require fairly high temperatures before decomposition, temperatures in the order of 700 to 900 C being required before significant cleavage of poly-carbon atom compounds is noted.¹

¹ B. T. Brice, W. H. Pearlson, and J. H. Simmons, "Fluorocarbon Chemistry: Cleavage of Carbon--Carbon Bonds by Chlorine and Bromine," Journal of the American Chemical Society, 71 (1949) pp. 2499-2501.

Appendix D, Exhibit 1APPENDIX DTest Apparatus and Procedure

EXHIBIT 1. Flame Inhibition Apparatus and Test Procedures at PRF. The apparatus used in the flame inhibition tests at PRF was as follows:¹

An apparatus similar in design to that described by Jones and Gilliland² was constructed for use in determining the flammable areas for mixtures of air, n-heptane and halogen compounds. This apparatus (see Fig. 4.) consisted of a combustion tube (1), 5.1 cm by 123 cm provided with suitable inlets for introducing dry air (8, 7, 17), heptane (19, 21) and a halogen compound (20, 22). A ground glass cover plate at the bottom of the tube permitted operation at reduced pressures and served as relief valve in case of an explosion within the tube. A mercury pump, consisting of valves (5, 6, 13) and mercury reservoirs (4, 12), were provided for mixing the gases. The pump was actuated by air pressure and the pumping was controlled by a solenoid valve (9). Valves (10, 11) were used to control the flows. A vacuum pump (23) was used for evacuating the combustion tube prior to charging it with the halogen compound and heptane. The pressure in the tube was determined from a manometer consisting of ameter stock (2) and a mercury well (3). Electrodes (15) and coil (16) were used to provide a spark for ignition. These electrodes were made from 24-gage platinum wire and adjusted to provide a spark gap of 6 mm. Little variation in the flammable limits was observed with changes in pressure from about 200 mm mercury to atmospheric pressures.

Since, in general, the vapor pressure of the test materials was too low at normal room temperature to permit the attainment of mixtures having the desired composition, it was found advantageous to carry out the experiments leading to the determination of flammable areas at pressures ranging from 300 to 500 mm of mercury. Hence, the combustion tube was evacuated and the desired amount of heptane and halogen compound was introduced, the compound with the lowest volatility being introduced first. Dry air was then introduced in sufficient quantity to produce the required total pressure.

¹ Purdue Research Foundation, Interim Report on Fire Extinguishing Agents for the Period 1 Sept 1947 to 1 March 1948, n.d., pp. 3-5.

² G. W. Jones, and W. Gilliland, Extinction of Gasoline Flames by Inert Gases. (U.S. Bureau of Mines, Report of Investigations, R. I. 3871, April 1946)

The composition of the mixture in the tube was calculated from the pressure of each component. The air, heptane and halogen compound was thoroughly mixed for a period of 10 to 15 minutes, the exact time depending upon the rate of pumping. Mixtures were considered flammable if the flame traveled from the spark gap to the top of the tube.

Techniques of operation were checked by determining the values for flammable limits of mixtures of benzene and air. The lower limit was found to be 1.4 to 1.6% and the upper limit 8.2 to 8.8% as compared with 1.4 and 8.0% previously determined at the Bureau of Mines (Bulletin 270, 1928). Limits of flammability for mixtures of heptane and air were determined at various total pressures. Greater precision was obtained when the flammable limits were determined at greatly reduced pressures.¹ For example, for mixtures containing 1 to 3% by volume of heptane, a total pressure of 500 mm of mercury was satisfactory, but when the heptane composition was of the order of 3 to 8%, more precise results were obtained when operating at a total pressure of 400 mm of mercury.

¹ Variations in the determination of the limits of flammability are believed to be due to the condensation of small quantities of heptane in the side-arm of the tubes before mixing was completed. As consequence, the composition of the mixture, as determined from the amount of material introduced, was not the true composition of the gaseous mixture. At the lower pressures, condensation in the side-arm is avoided and the composition of the gaseous mixture is more accurately obtained from the quantities of materials introduced. The flammable limits of heptane and air were found to be 1.0 to 1.2% for the lower limit and 7.0 to 7.3% for the upper limit.

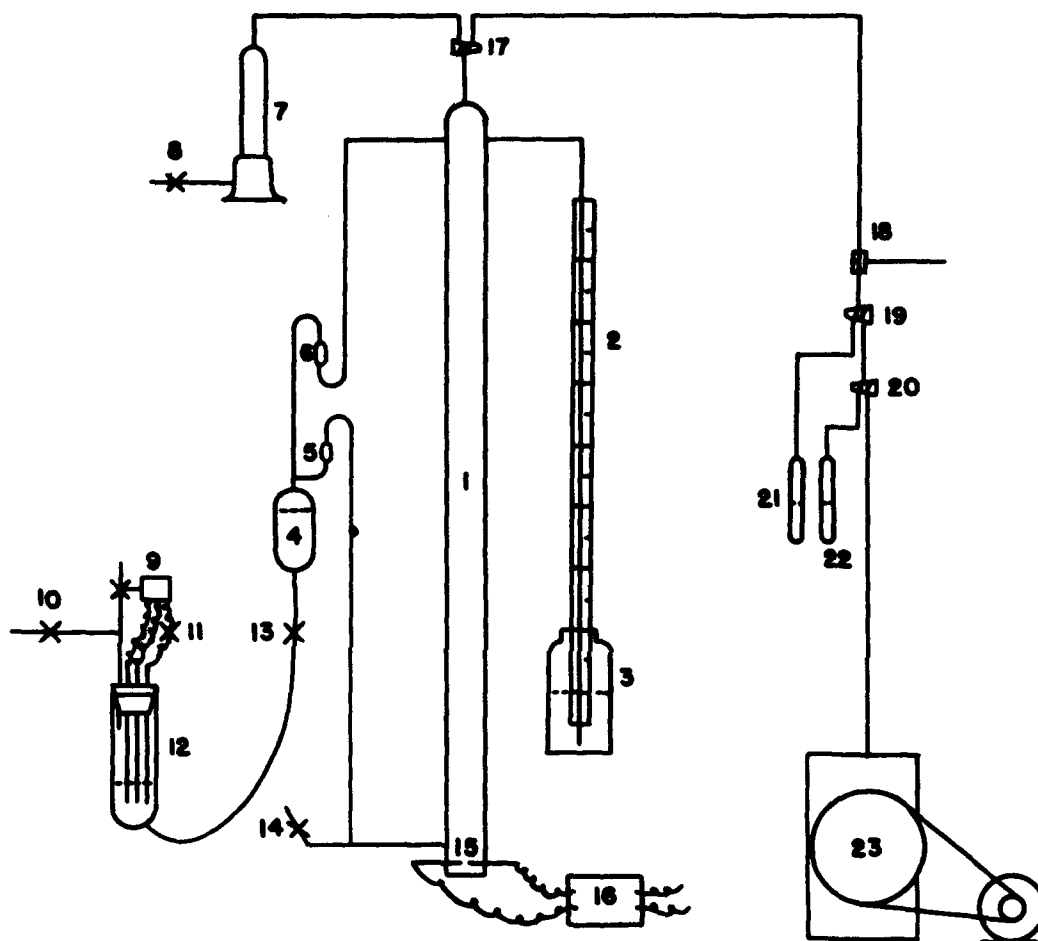


Fig. 4. Flame Inhibition Apparatus used at the Purdue Research Foundation.

Appendix D, Exhibit 2

EXHIBIT 2. Laboratory Apparatus and Procedure for EEDL Fire Extinguishment Tests. A laboratory setup (see Fig. 5.) was developed by the Materials Branch of the EEDL, by means of which the fire extinguishing agent could be applied at a constant rate through the fixed inlets (A) to the n-heptane fire in the water jacketed container (B). The agent vapors were passed through a small rotometer (C), and the flow rate was controlled by the pressure reducing valve (D). Prior to test, the agent vapor lines were purged with N_2 followed by the particular agent under test. In the test procedure followed, a flow of cold water was maintained in the container jacket (E) to insure a constant temperature, and the container was filled with n-heptane to within exactly one inch of the fixed inlets. After the heptane had been ignited with a gas burner, a preburn of 30 seconds was permitted, following which, the agent vapors were admitted to the test container at a predetermined and constant pressure (constant flow rate), and the time of extinguishment was noted by a stop watch. Finally, the jacketed container, which was located under a laboratory hood, was flushed with fresh air. The amount of agent required could be calculated from the time and rate of flow, and various rates were used to determine if this variable affected the results significantly. This method was adaptable only to compounds which are gases at room temperature and pressure.

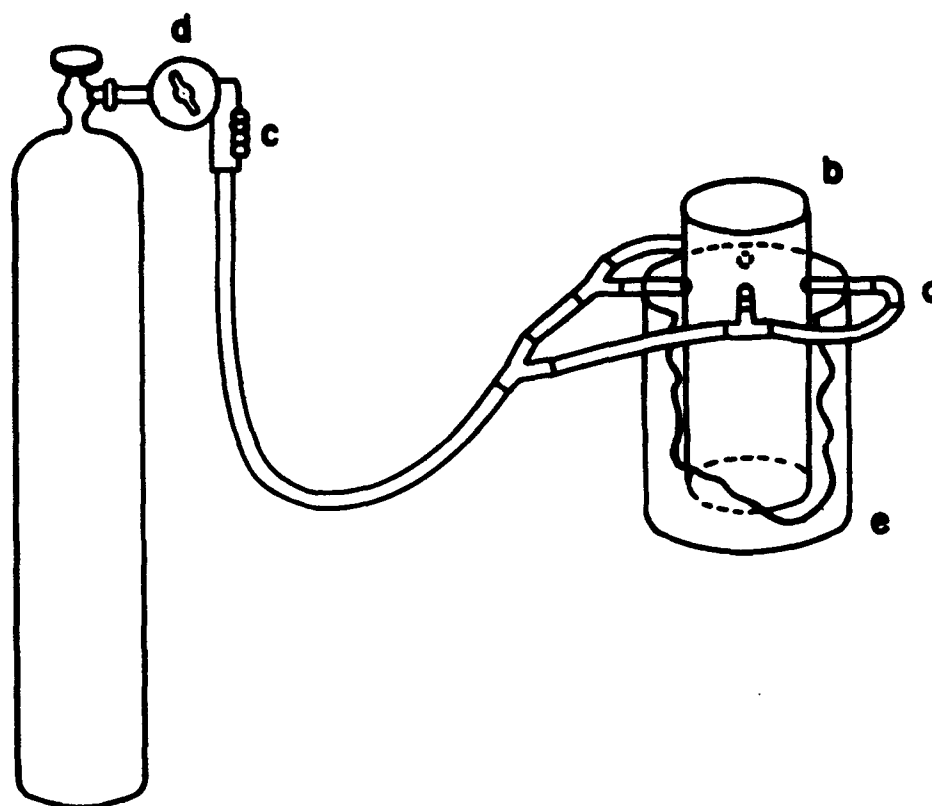


Fig. 5. Pot fire test apparatus used at the ERDL.

Appendix D, Exhibit 3

EXHIBIT 3. Modified Flame Inhibition Apparatus for Study of Temperature Effects at PRF. This apparatus was essentially the same as that used in the flammability determinations, except that the combustion tube was placed in an insulated cylinder bath that could be heated electrically to control the tube temperature within 1 degree Centigrade or could be cooled by dry ice in trichloroethylene. Some changes were necessary in the tube (the stopper serving as a relief valve had to be placed on the top of the tube). This apparatus is described as follows:¹

As with conventional tubes, a pyrex tube (51 mm OD by 120 cm long) was constricted and an 8-mm tube was sealed at the end to lead to the mixing system. The edge of the open end was ground smooth and flat so as to make a tight seal with a flat piece of rubber when the tube was evacuated. An 8-mm tube leading from the mixing system was sealed to the tube through a ring-seal near the open end. A spark gap was made by sealing two platinum electrodes in the tube near the closed end. The experiments were then performed by placing the tube either in a bath of dry ice and trichloroethylene for the -78 C data an air bath for room temperature data and an oil bath heated by two 75-watt heaters (No. 19 Nichrome) controlled through 18-amp variacs for the +145 C data. It was necessary to use a pumping cycle of 30 minutes to insure complete homogeneity of the gaseous mixtures.

¹ Purdue Research Foundation, Interim Report on Fire Extinguishing Agents for the Period 1 March 1949 to 31 August 1949, n.d., p 14.

Appendix D, Exhibit 4EXHIBIT 4. PRF Data on Effect of Temperature and Pressure on Various Agents.

<u>Fig.</u>	<u>Title</u>	<u>Page</u>
6	Effect of temperature on flammable area of bromomethane, Top: at +26 C; Bottom: at -78 C.	62
7	Effect of temperature on flammable area of carbon tetrafluoride, Top: at +26 C; Bottom: at -78 C.	63
8	Effect of temperature on flammable area of chlorotrifluoromethane, Top: at +26 C; Bottom: at -78C.	64
9	Effect of temperature on flammable area of bromotrifluoromethane, Top: at +26 C; Bottom: at -78 C.	65
10	Effect of temperature on flammable area of sulfur hexafluoride, Top: at +26 C, Bottom: at -78 C.	66

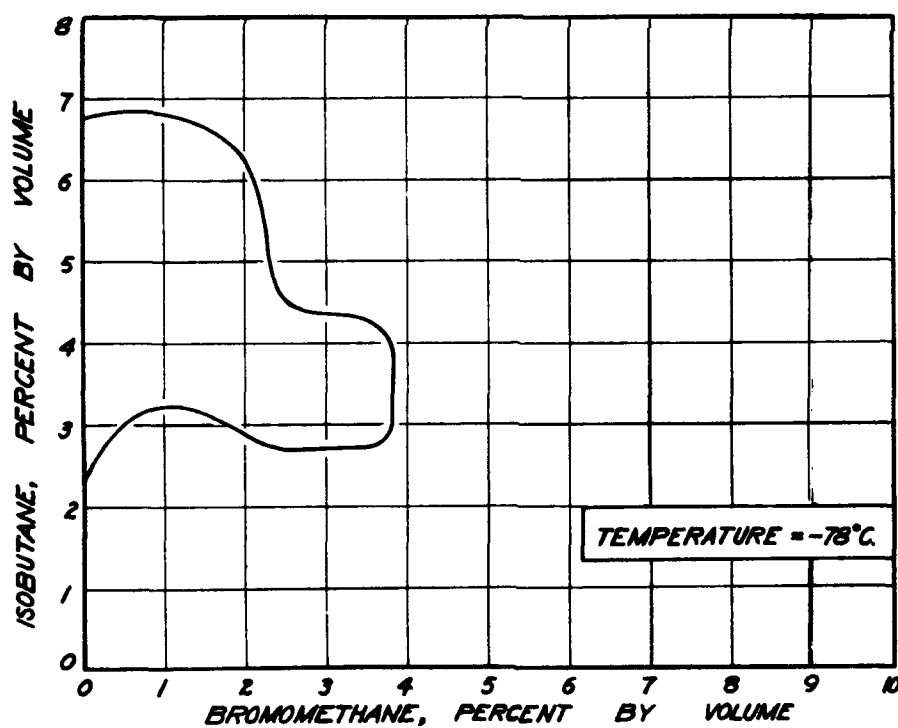
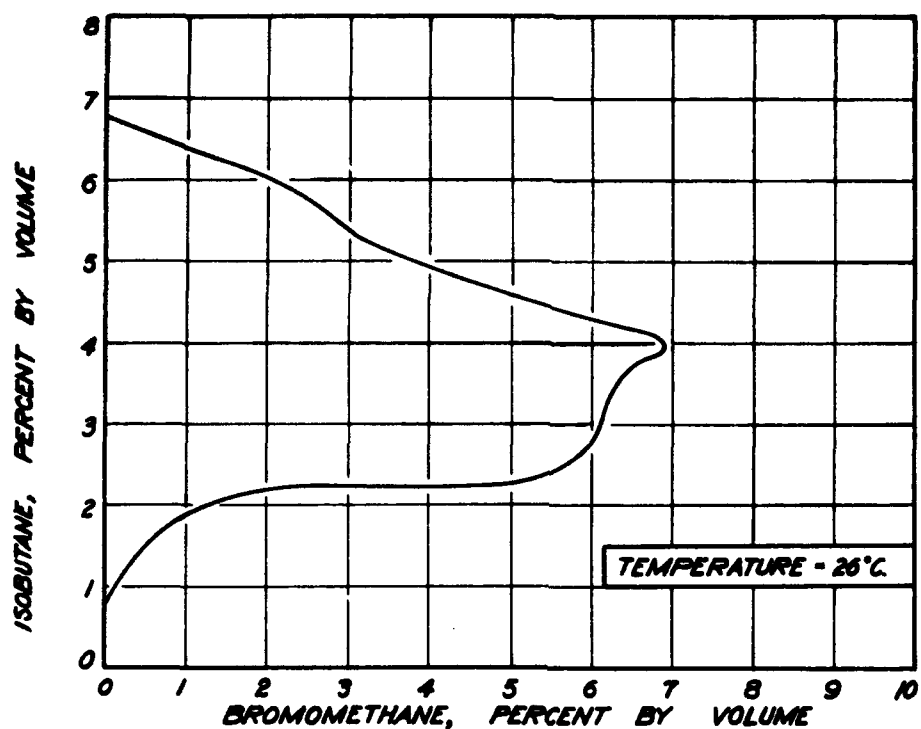


Fig. 6. Effect of temperature on flammable area of bromomethane, Top: at +26 C; Bottom: at -78 C.

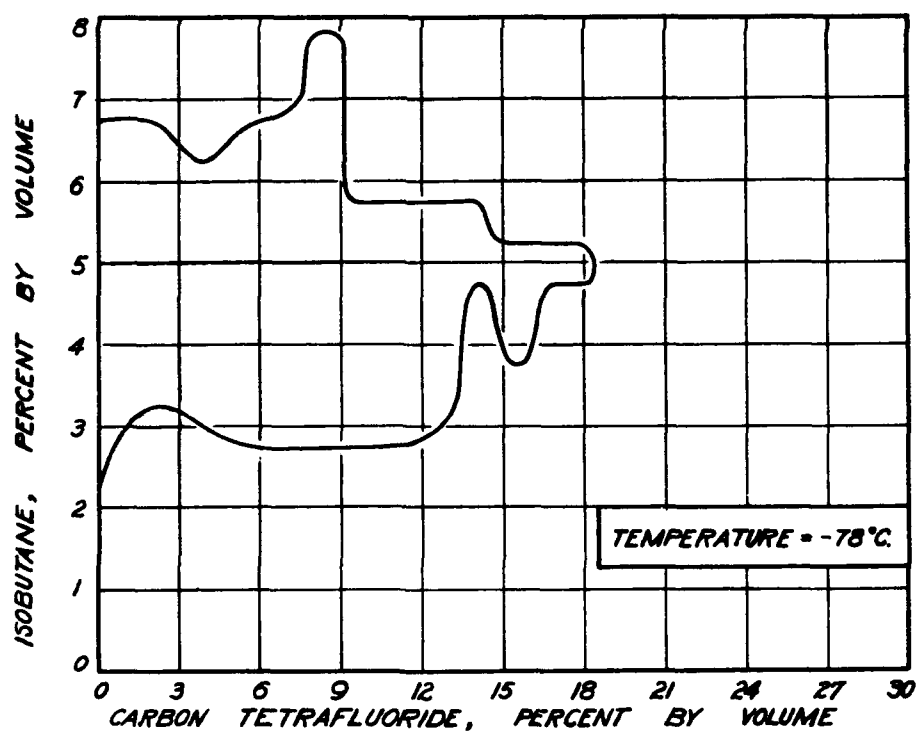
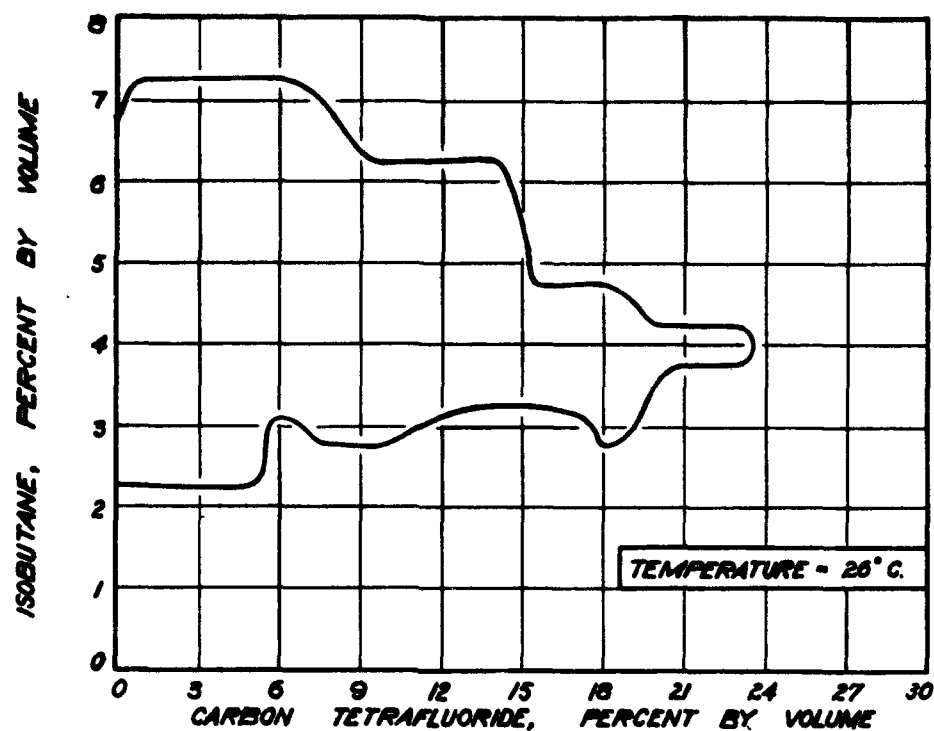


Fig. 7. Effect of temperature on flammable area of carbon tetrafluoride, Top: at +26 C; Bottom: at -78 C.

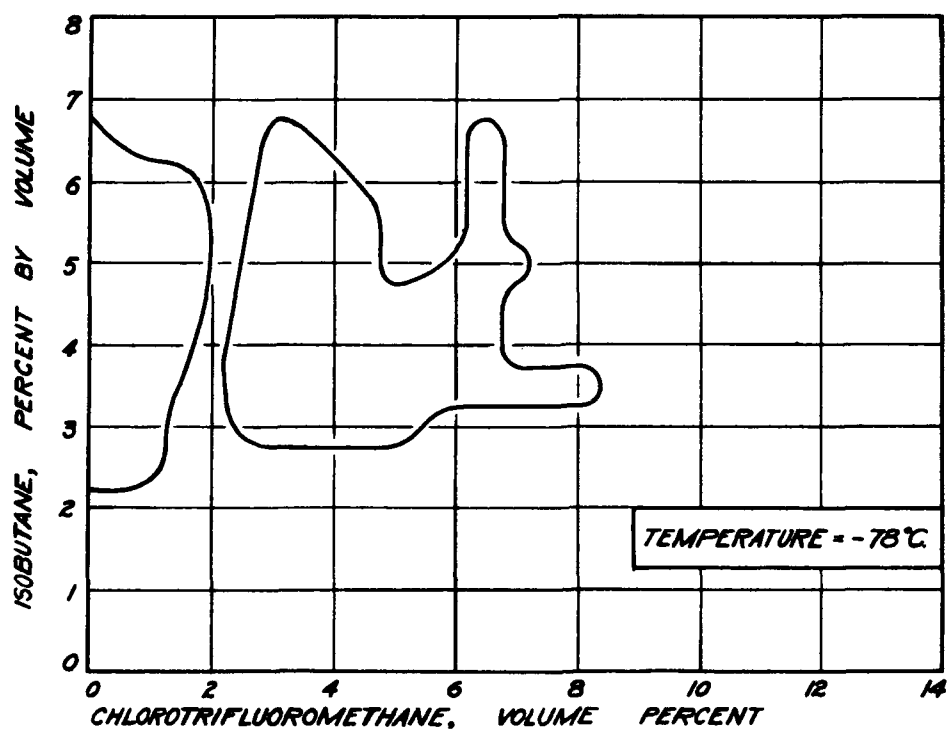
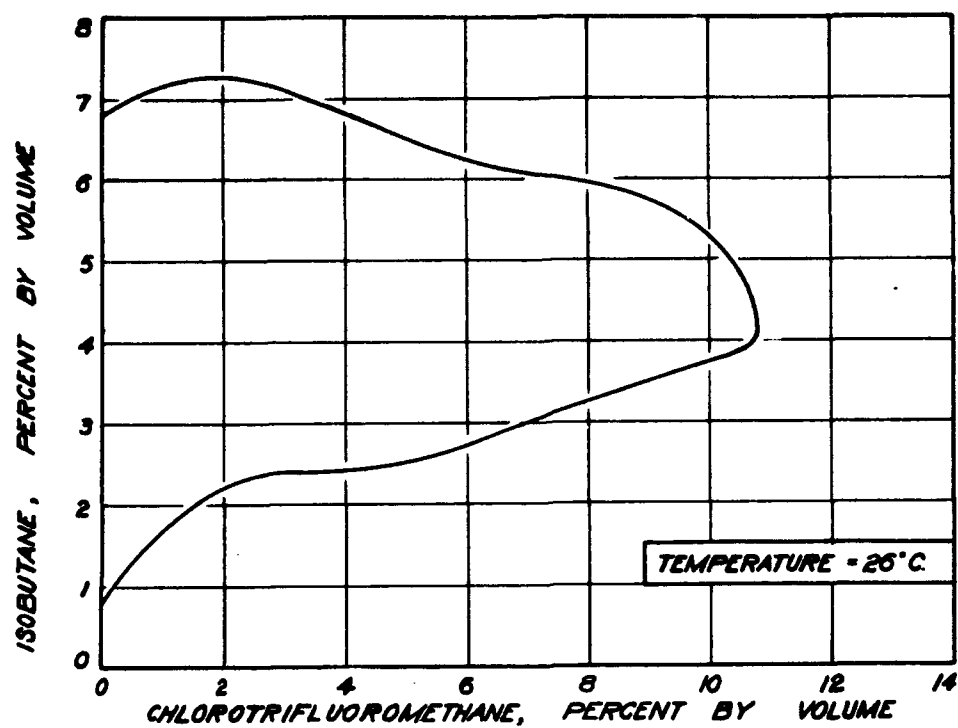


Fig. 8. Effect of temperature on flammable area of chlorotri-fluoromethane, Top: at +26 C; Bottom: at -78 C.

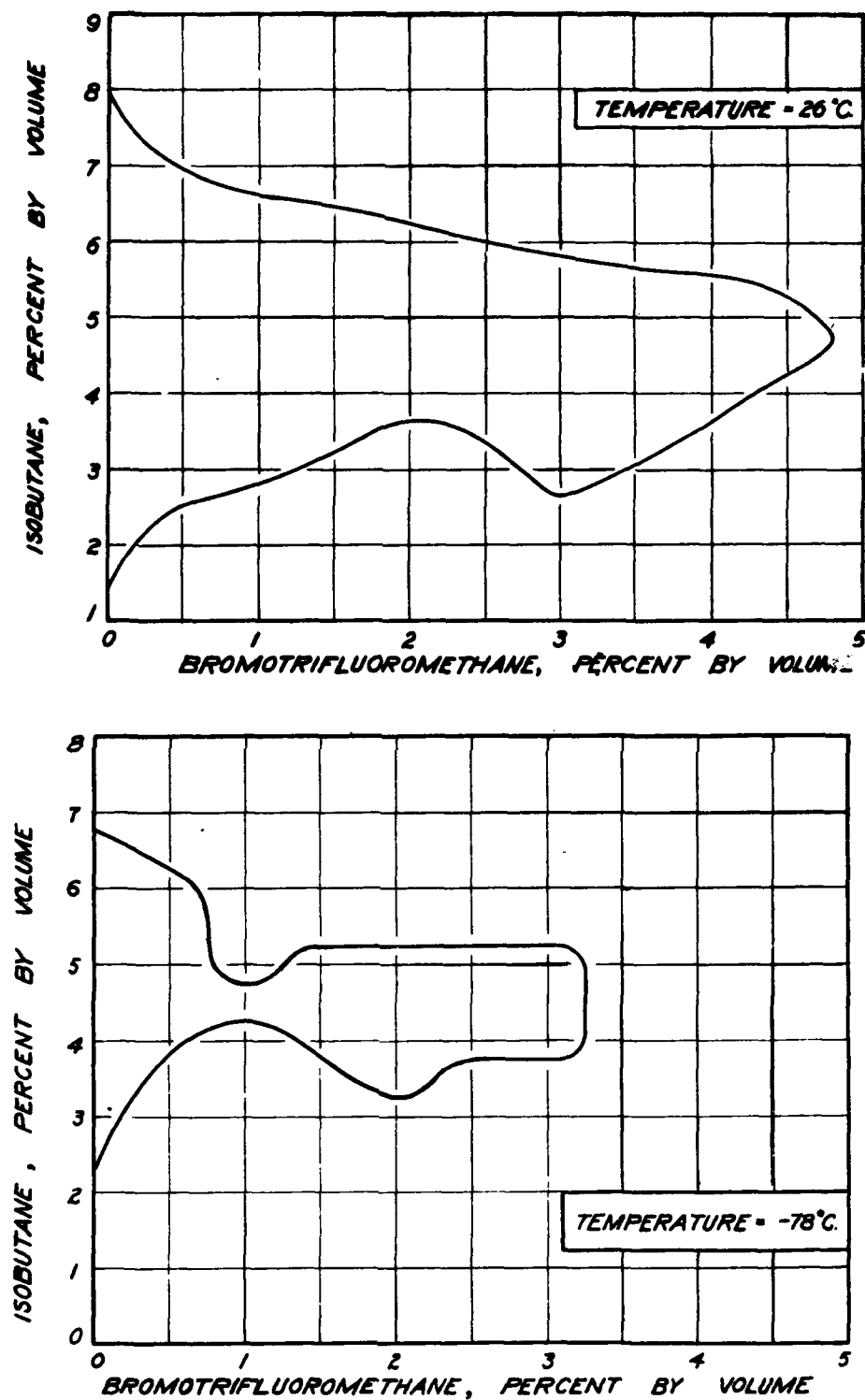


Fig. 9. Effect of temperature on flammable area of bromotrifluoromethane, Top: at -26°C ; Bottom: at -78°C .

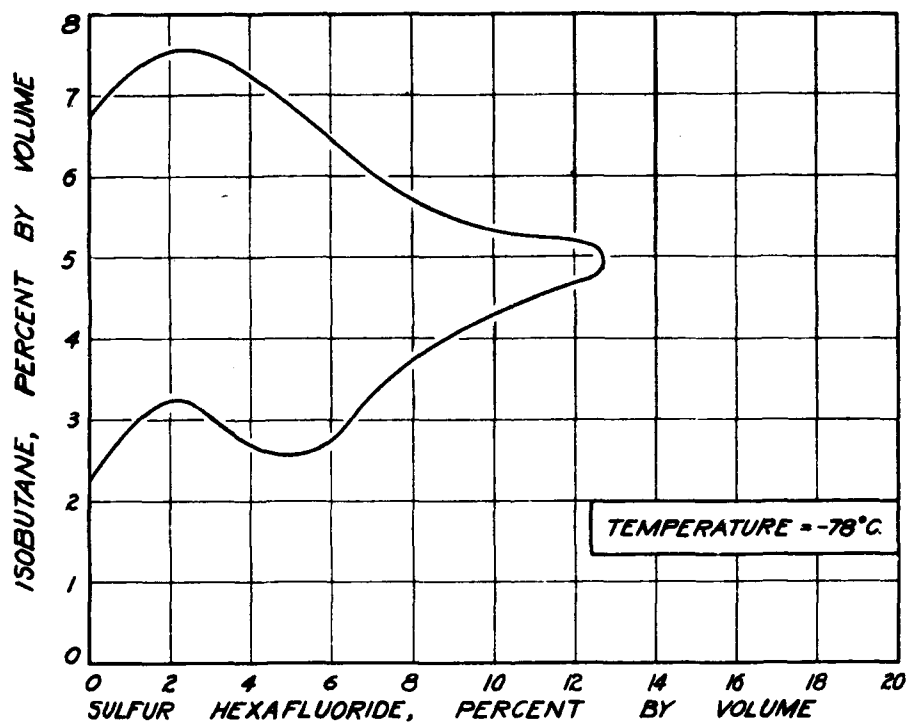
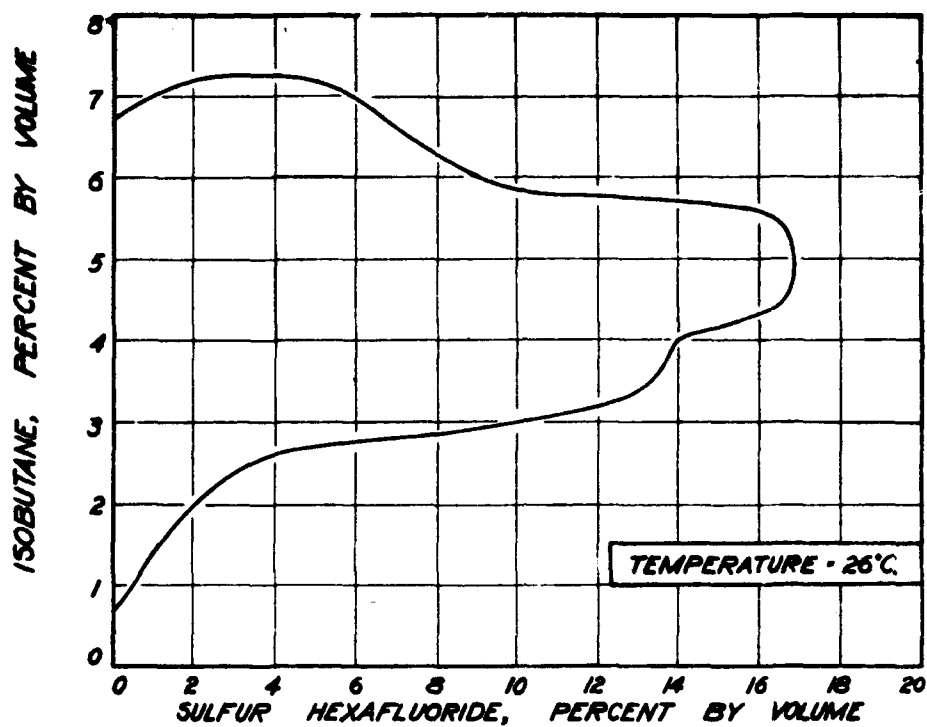


Fig. 10. Effect of temperature on flammable area of sulfur hexafluoride, Top: at +26 C, Bottom: at -78 C.

Appendix D, Exhibit 5

EXHIBIT 5. Apparatus and Procedures for Corrosion Tests at PRF¹. Polished and weighed strips of metal and 20 ml of the halogen compound were sealed in ampoules (Carius tubes). The weight of the samples varied from 1.2 to 3.5 g, depending on the type of metal. The tubes were inserted in iron pipes which, in turn, were placed in an oven heated at 392 F. After 30 days, the tubes were allowed to cool to room temperature and then opened. The physical appearance of each strip was noted and the liquid contents were stored in vials for future studies. After removing coatings from the strips which had corroded, the strips were reweighed and changes in weight compared with the original value were recorded. This study was initiated to show the stability of halogen compounds to aluminum, copper and iron, common materials of construction. After this study was initiated it was requested that brass strips be substituted for copper strips.

Compounds showing marked instability to the metals at 392 F, were heated in contact with the same metals at 200 F. In addition, experiments were conducted in which the halogen-containing compounds were heated in contact with magnesium ribbon at 200 F.

¹ Purdue Research Foundation, Summary Report on Fire Extinguishing Agents for the Period September 1, 1947 to August 31, 1948, n.d., p 13.

Appendix D, Exhibit 6EXHIBIT 6 Corrosion Data Obtained by PRFTable XVIII. Corrosive Action at Reflux Temperature,
under Aqueous Conditions for 100 Hours

Compound	Weight of Metals (g)		Change in Weight	
	Original	Final	g	%
Carbon Tetrachloride				
Copper	1.8449	1.7271	-0.1178	- 7
Aluminum	1.2891	0.0000	-1.2891	-100
Iron	3.4522	2.4549	-0.9973	- 29
Carbon Tetrachloride (with inhibitor)				
Copper	1.8289	1.7306	-0.0983	- 5
Aluminum	1.2921	0.0000	-1.2921	-100
Iron	3.2768	2.1348	-1.1420	- 32
Bromochloromethane				
Copper	1.7705	1.7652	-0.0053	nil
Aluminum	1.3454	0.0000	-1.3454	-100
Iron	3.4169	2.8851	-0.5308	- 16

Table XIX. Corrosive Action at 392 F (200 C) for 30 Days

Compound	Weight of Metals (g)		Change in Weight		Appearance
	Original	Final	g	%	
Carbon Tetrachloride (with inhibitor)					
Copper	1.8297	0.0000	-1.8297	-100	Completely corroded
Aluminum	1.1894	0.0000	-1.1894	-100	Completely corroded
Iron	3.0947	0.0000	-3.0947	-100	Completely corroded
Carbon Tetrachloride (without inhibitor)					
Copper	1.7005	0.0000	-1.7005	-100	Completely corroded
Aluminum	1.4000	1.3567	-0.0433	-3	Gray coating
Iron	2.8319	2.7562	-0.0757	-3	Black coating
Dichloromethane					
Copper	1.7005	0.0000	-1.7005	-100	Black, completely corroded
Aluminum	1.4190	1.3393	-0.0797	-6	Black coating
Iron	3.1027	3.0785	-0.0242	-8	Black coating
Bromochloromethane					
Copper	1.8078	0.0000	-1.8078	-100	Completely corroded
Aluminum	1.1758	0.6501	-0.5257	-45	Corroded
Iron	2.7196	2.7351	+0.0156	+1	Red coating
Dibromomethane					
Copper	1.7856	0.0000	-1.7856	-100	Completely corroded
Aluminum	1.1824	0.7041	-0.4783	-40	Corroded
Iron	3.2240	3.1121	-0.1119	-34	Red coating
1,1,2-Trichlorotri-fluoroethane					
Copper	1.8443	0.9085	-0.9358	-51	Gray coating
Aluminum	1.1920	1.1920	0.0000	0	Slight discoloration
Iron	3.0530	3.0530	0.0000	0	Slight discoloration
1-Bromo-2-chloro-ethane					
Copper	1.7457	0.7730	-0.9727	-60	Black coating
Aluminum	1.4380	1.3188	-0.1192	-8	Black coating
Iron	3.2271	3.1982	-0.0289	-1	Black coating

Table XIX (Continued)

Compound	Weight of Metals, (g)		Change in Weight		Appearance
	Original	Final	g	%	
1,2-Dibromotetrafluoroethane					
Copper	1.7443	1.5442	-0.2001	-11	Gray coating
Aluminum	1.4465	0.0000	-1.4465	-100	Gray, completely corroded
Iron	2.9080	2.9043	-0.0037	nil	Black coating
3-Bromo-1,1,1-trifluoropropane					
Copper	1.7581	1.6965	-0.0616	-3	Gray coating
Aluminum	1.2280	1.2280	0.0000	0	No discoloration
Iron	3.1935	3.1841	-0.0094	nil	No discoloration
2-Bromo-1,1,1-trifluoropropane					
Copper	1.6717	1.5705	-0.1012	-6	Black coating
Aluminum	1.3970	0.0000	-1.3970	0	Completely corroded
Iron	3.2663	3.2510	-0.0153	nil	Black coating
Perfluoroheptane					
Copper	1.6055	1.6055	0.0000	0	No change
Aluminum	1.4428	1.4601	+0.0173	0	Slight tarnish
Iron	2.7258	2.7258	0.0000	0	No change
Perfluoroethylcyclohexane					
Copper	1.6861	1.6861	0.0000	0	No change
Aluminum	1.4149	1.4327	+0.0178	0	Slight tarnish
Iron	3.1050	3.1050	0.0000	0	No change
Perfluoro(1,3-dimethylcyclohexane)					
Copper	1.6838	1.6854	+0.0016	nil	Slight tarnish
Aluminum	1.3945	1.4041	+0.0096	+1	Slight tarnish
Iron	2.8250	2.8256	+0.0006	nil	Slight tarnish
Perfluoro(1,4-dimethylcyclohexane)					
Copper	1.7371	1.7371	0.0000	0	No change
Aluminum	1.3883	1.4062	+0.0179	+1	Slight tarnish
Iron	3.1313	3.1318	+0.0005	nil	No change
Perfluoromethylcyclohexane					
Copper	1.6209	1.6209	0.0000	0	No change
Aluminum	1.4828	1.5062	+0.0234	+2	Slight tarnish
Iron	2.9908	2.9908	0.0000	0	No change

Table XIX. (Continued)

Compound	Weight of Metals (g)		Change in Weight		Appearance
	Original	Final	g	%	
Perfluoronaphthalene					
Copper	1.7350	1.7350	0.0000	0	No change
Aluminum	1.4029	0.0000	-1.4029	-100	Black, completely corroded
Iron	2.9379	2.9379	0.0000	0	No change
Perfluoroindane					
Copper	1.6678	1.6678	0.0000	0	No discoloration
Aluminum	1.4031	1.4175	+0.0144	+1	Black coating
Iron	3.8083	3.1083	0.0000	0	No discoloration
Methyl bromide					
Copper	1.8437	1.8698	+0.0261	+1	Slight discoloration
Aluminum	1.2145	1.2145	0.0000	0	No discoloration
Iron	2.8084	2.8130	+0.0046	nil	Slight discoloration
Trifluoromethane (fluoroform)					
Copper	1.7830	1.7830	0.0000	0	No discoloration
Aluminum	1.2572	1.2572	0.0000	0	No discoloration
Iron	3.1043	3.1043	0.0000	0	No discoloration
Bromotrifluoromethane					
Copper	1.8290	1.8398	+0.0108	+1	Slight discoloration
Aluminum	1.2101	1.2110	+0.0009	nil	No discoloration
Iron	3.1116	3.1170	+0.0054	nil	Slight discoloration
Chlorotrifluoromethane					
Copper	1.8625	1.8625	0.0000	0	No discoloration
Aluminum	1.1830	1.1830	0.0000	0	No discoloration
Iron	2.9177	2.9177	0.0000	0	No discoloration

Table XX. Corrosive Action at 200 F (93 C) for 30 Days

Compound	Weight of Metals (g)		Change in Weight		Appearance
	Original	Final	g	%	
Carbon Tetrachloride					
Copper	1.8331	1.7821	-0.0510	-3	Black coating
Aluminum	1.2198	0.6177	-0.6021	-49	Black coating
Iron	3.3224	3.2718	-0.0506	-2	Red coating
Carbon Tetrachloride (with inhibitor)					
Copper	1.8828	1.5780	-0.3048	-16	Black coating
Aluminum	1.1596	0.0000	-1.1596	-100	Completely corroded
Iron	3.3024	2.7677	-0.5347	-14	Red coating
1-Bromo-2-chloroethane					
Copper	1.7733	1.7485	-0.0248	-1	Black coating
Aluminum	1.2397	0.0000	-1.2397	-100	Completely corroded
Iron	3.2377	3.2255	-0.0122	nil	Black coating
2-Bromo-1,1,1-trifluoro- propane					
Copper	1.8174	1.8174	0.0000	0	No discolor- ation
Aluminum	1.3880	1.3880	0.0000	0	No discolor- ation
Iron	3.6006	3.6006	0.0000	0	No discolor- ation
1,2-Dibromotetrafluoro- ethane					
Copper	1.8552	1.8552	0.0000	0	No discolor- ation
Aluminum	1.1781	1.1781	0.0000	0	No discolor- ation
Iron	3.4582	3.4582	0.0000	0	No discolor- ation

Appendix D, Exhibit 7

EXHIBIT 7. Apparatus and Procedures, Toxicity Screening of Halocarbons by Army Chemical Center. Fire extinguishing agents were used as follows:

<u>Agent</u>	<u>Formula</u>	<u>Halon No.</u>
Carbon Tetrachloride	CCl_4	104
Chlorobromomethane	CH_2ClBr	1011
Methyl bromide	CH_3Br	1001
Bromotrifluoromethane	CF_3Br	1301
Dibromodifluoromethane	CF_2Br_2	1202
Dibromotetrafluoroethane	$\text{C}_2\text{F}_4\text{Br}_2$	2402
Dibromochlorotrifluoroethane	CF_3ClBr_2	2312
Ethyl bromide	$\text{C}_2\text{H}_5\text{Br}$	2001
Perfluoromethylcyclohexane	$\text{C}_6\text{F}_{11}\text{CF}_3$	GN(M)
Carbon tetrafluoride	CF_4	14

Carbon dioxide (CO_2) was used for purposes of comparison. The animals used were male Wistar strain rats weighing between 220 and 250 g.

For undecomposed vapor, glass constant-flow gassing chambers of 20-liter capacity were used. The air flow through the chambers was held constant at the rate of 2 liters per minute. Concentrations of the compound to be examined were set up by introducing measured quantities of vapor into the affluent air at a constant rate. A number of exposure runs were made using concentration levels, each 50 percent higher than the previous run. One rat was exposed in each run for 15 minutes. Survivors were observed for 14 days. Dead animals were examined for pathology. The time for anesthesia during exposure was noted.

For pyrolyzed vapor the procedure was the same as that for natural vapor, with the exception that prior to introduction into the gassing chamber the vapors were passed through an iron pipe maintained at 800 C in an electric furnace and then cooled to room temperature. The rate of flow through the heated pipe was adjusted so that the vapors were in contact with the hot metal for one second.

The method proposed by Deichmann¹ was used as a basis for calculation of results. Deichmann administered to single animals doses

¹ W. B. Deichmann and T. J. LeBlanc, "Determination of the approximate Lethal Dose with about Six Animals," J. Ind. Hyg., 25 (1943,) p. 415.

graded so that they were increased by 50 percent. The dose causing the first death was called the "approximate lethal dose" (ALD). Since this method had not previously been used for inhalation studies, its validity was partially verified by an experimental series of runs with methyl bromide, using 10 rats at each concentration level, the results being calculated by the method of Wilcoxon and Litchfield². In the calculation of the "approximate lethal concentration" (ALC), all deaths occurring from the time of exposure to the end of the 14-day observation period were used.

² F. Wilcoxon and J. T. Litchfield, Jr., "A Simplified Method for Evaluating Dose-Effect Experiments," J. Pharm. and Exptl. Ther., 96, 2, (June 1949), pp 99-113.

Appendix D, Exhibit 8

EXHIBIT 8. Engineering Test Apparatus and Procedures. The Randolph Laboratories' 2 $\frac{1}{2}$ -lb CO₂ unit was used for applying the agents in the engineering tests, while the fuel used was unleaded industrial naphtha. Basically the test procedures followed Underwriters' Laboratory standards.

a. Class B Fires. In the 2-ft diameter tub fires, a 2-ft diameter tub of sheet steel was filled with water to within 10 $\frac{1}{2}$ inches of the rim. Two quarts of gasoline were poured on the water and ignited. A preburn of 20 seconds was allowed before the fire was attacked as shown in Fig. 11.

b. Class C Fires. Three Class C fire tests were used: (1) Eight pounds of cotton waste were spread over an area measuring 2 by 4 feet, wetted evenly with 2 quarts of gasoline, and ignited. After a 10-second preburn, the fire was attacked from one narrow end of the area, toward the other. (2) The second test was conducted in the same manner as the first except that 6 pounds of waste were placed in an area 2 by 3 feet, and 1 $\frac{1}{2}$ quarts of gasoline were applied. (3) In the third test, 4 pounds of cotton were used in an area 2 by 2 feet and 1 quart of gasoline was applied (see Fig. 11). The bulk of the Class C fire tests were conducted with the first procedure cited above, since this procedure proved most suitable for obtaining data on the more effective fire extinguishing agents, and these data are shown in Table XXI.



Fig. 11. Top: Extinguishing Class B tub fire with dibromodifluoromethane, Bottom: Extinguishing Class C cotton waste fire with the same agent.

Appendix B, Exhibit 9EXHIBIT 9. Data, Engineering Test, (NVAL)

Table XII. Evaluation of Horn and Orifice Effects on
the Effectiveness of Dibromodifluoromethane
in Class B 2-ft Tub Fire Tests^a

Horn Dimensions ^b	Orifice Diameter (in.)	Ext. (oz)	Approx. Time to Ext. (Sec)
1 13/16-in. diam by 5-in. long	0.0625	9.6	2
" " " " "	0.0442	8.6	3
" " " " "	0.0284	5.6	5
1 13/16-in. diam by 2 1/2-in. long	0.0625	8.3	2
" " " " "	0.0442	5.3	2
" " " " "	0.0284	3.3	3
3-inch. max. diam flare	0.0625	11.3	3
" " " " "	0.0442	7.6	3
" " " " "	0.0284	7.3	7

(a) Tests conducted with 2 1/2-lb CO₂ cylinders containing 2 lb of agent pressurized to 400 psig at 70 F with nitrogen. Results indicated are averages of 3 tests.

(b) See Fig. 12.

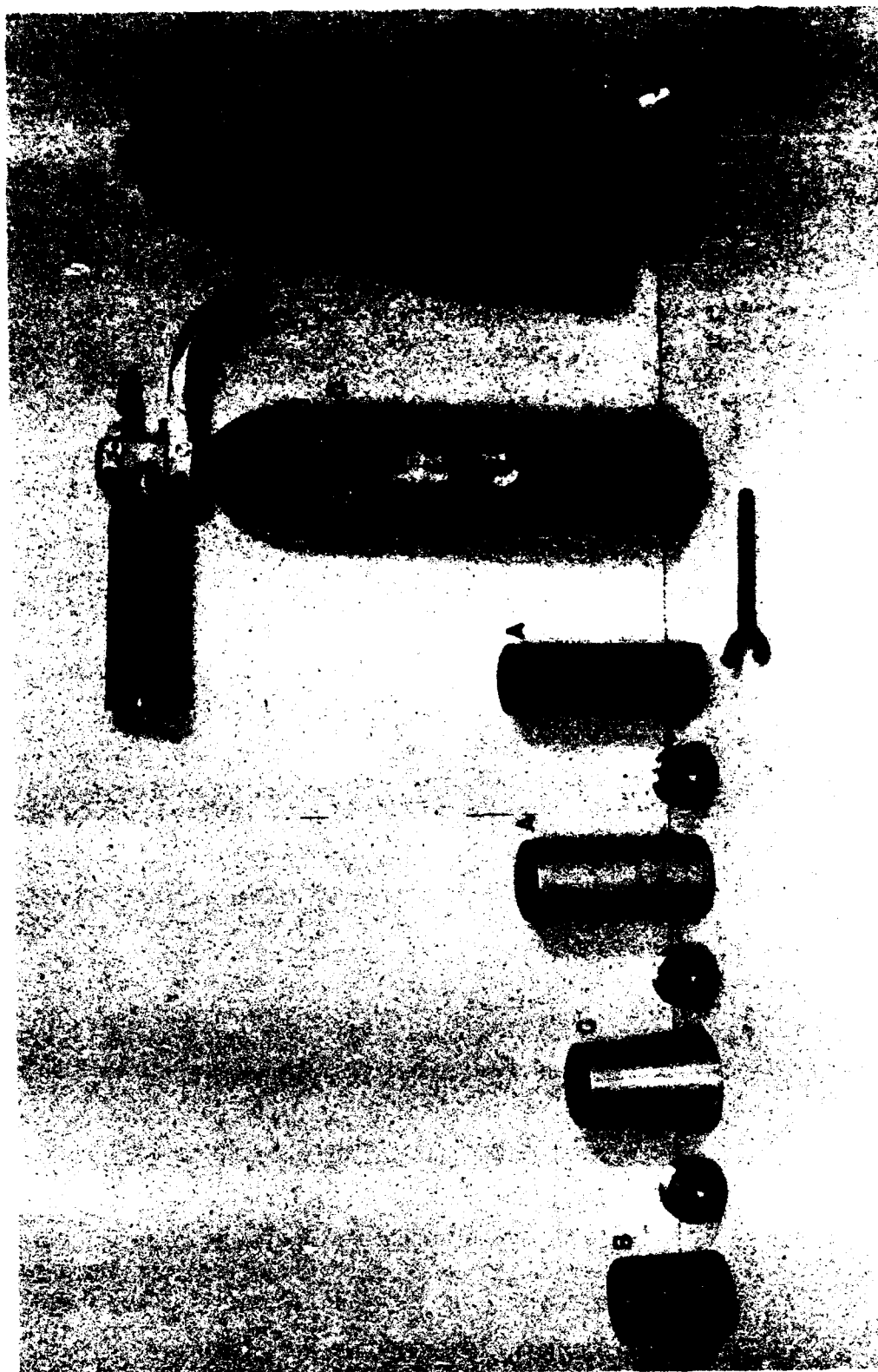


Fig. 12. Horns (used on Randolph and C-0-Two extinguishers) employed in RFDL fire tests. (A) 1 13/16 in. diam by 5 in. long; (B) 1 13/16 in. diam by 2 1/2 in. long; (C) 3 in. maximum diam flare.

Appendix D, Exhibit 10

EXHIBIT 10. Apparatus and Procedures, Low Temperature Fire Tests in ERDL Cold Chamber. In conducting fire tests at -65 F, it was necessary to use the large (14- by 13- by 38-ft) Cold Chamber of the ERDL Climatic Test Laboratory, where an exhaust fan of 3600 cfm capacity is available. In order to contain the test fires, as well as to collect and exhaust the combustion products immediately, a special test canopy measuring 8 by 6 by 6 $\frac{1}{4}$ feet (see Fig. 13) was designed by the Fire Apparatus Section and constructed in the ERDL Shops. By the use of this device, danger to personnel was avoided, and the atmosphere was kept clear enough so that the test fires could be observed.

Equipment was set up in the test canopy and in the control room to provide semi-automatic and remote control of the tests. The equipment in the canopy is shown in Fig. 14. An oscillating swivel arm (A) was provided to direct the spray from the test cylinder (B) over the entire surface of the 25-in. square burning pan (C), in which a spark plug (D) and methane bleed line (E) were provided to ignite the fuel. A photo-electric cell (F) was provided to record the incidence of fire in the pan. Since the cell is normally inoperative at -65 F, it was placed in an insulated box with a 20-watt light bulb to insure proper operation, a thermocouple located in the insulated box indicated that a temperature of 50 F was maintained throughout the tests. The impulse from the photo-electric cell operated through a time delay relay to activate a motion picture camera covering the field indicated in Fig. 14. The time delay relay also activated the solenoid (G) and the oscillating motor (H), the units that provided for the release of the extinguishing agent and the sweep of the extinguisher over the burning pan. The rheostat (J) controlled the period of oscillation, which in these tests, was held at 5 $\frac{1}{2}$ seconds for a complete cycle. The impulse from the photo-electric cell resulting from the extinguishment of the fire was converted by the relay box to the necessary circuit changes to immediately close the extinguisher valve, cease oscillation of the bracket arm, and stop the motion picture camera. An electric clock was synchronized with the relay box so as to indicate the time required for extinguishment.

Thermocouples located inside the Cold Chamber indicated the test temperature.

Randolph Laboratories 2 $\frac{1}{2}$ -lb and C-O-Two 2-lb CO₂ extinguishers, charged with 2 pounds of agent, were used for the tests. An aluminum horn was used for all the spray application tests and a straight stream commercial nozzle was used with the same cylinder for the straight stream application tests.

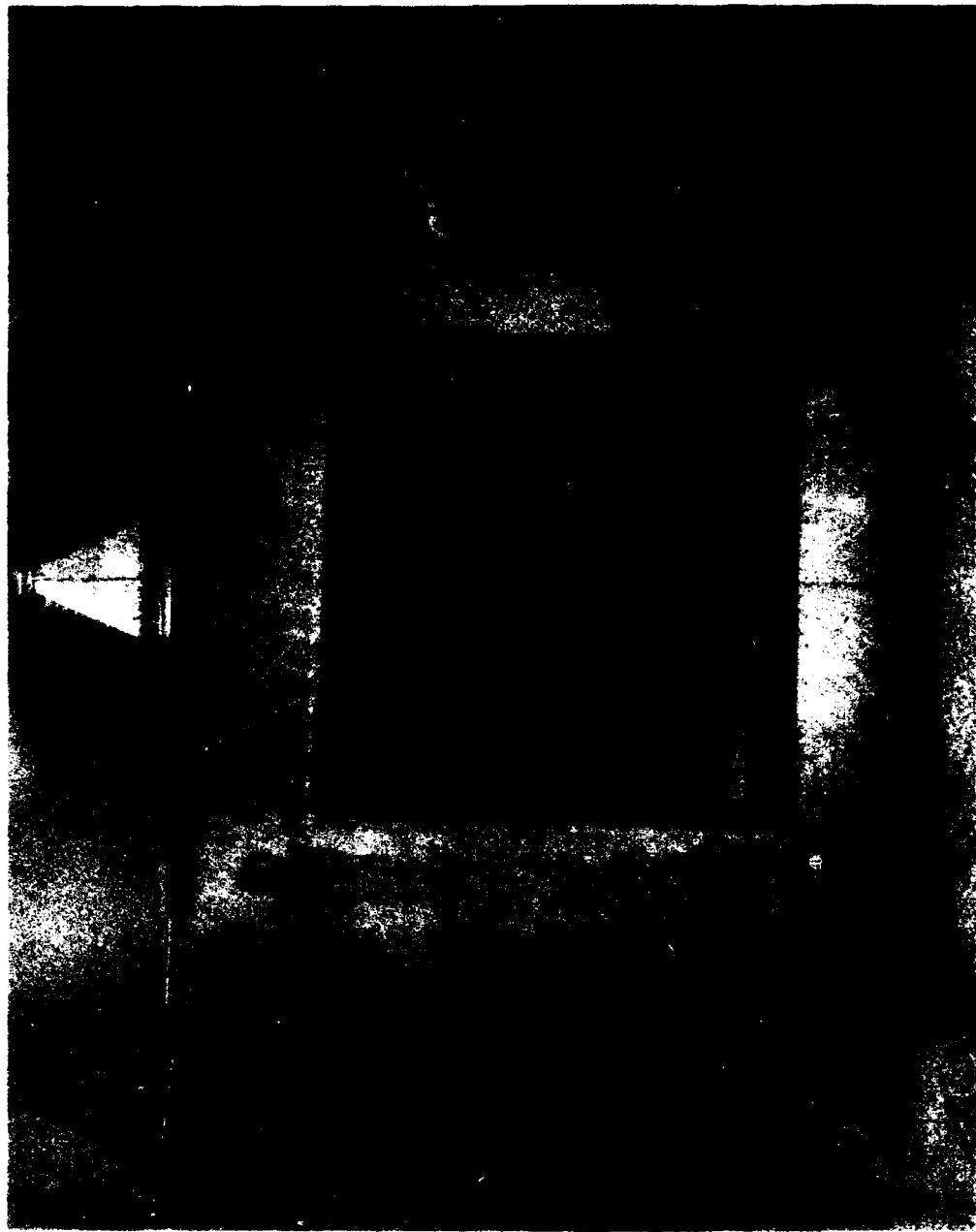


Fig. 13. Canopy used in Cold Chamber tests of fire extinguishing agents. (A) oscillating horn; (B) burning pan; (C) spark plug; (D) housing for operating mechanism; (E) exhaust vent; (F) auxiliary observation window (side of canopy was open, as shown here, during tests).

The test procedure was as follows:

Each charged extinguisher was weighed before and after test, and the weights were recorded.

Prior to each fire 8 oz of fuel was placed in the burning pan.

During the first tests the fire was started by activating the spark plug; however, the plug became so badly fouled that subsequently the fire had to be lighted manually.

The time interval between ignition of the fire, and activation of the extinguisher by the time delay relay was measured by a manually operated stop watch, and was recorded.

The time required for extinguishment was indicated automatically on an electric clock, and was recorded by the operator, as was the method of applying the agent (straight stream or mist), and the number and type of cylinder used.

Care was taken to insure that no agent remained in the burning pan before undertaking a subsequent test.

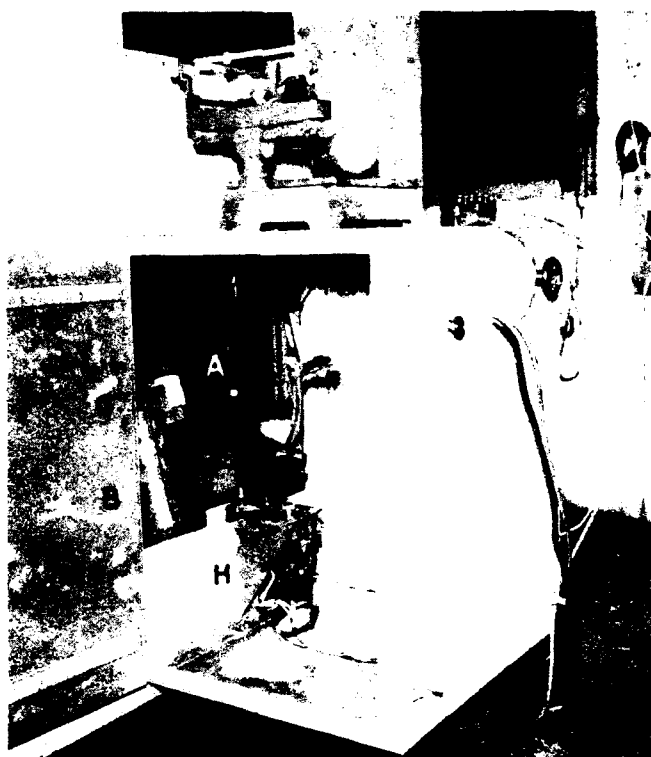
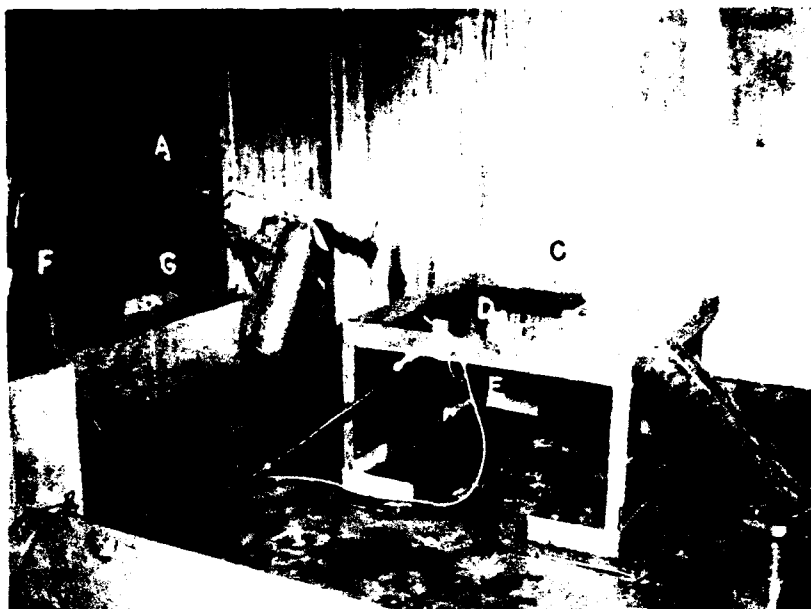


Fig. 14. Interior and controls of canopy used in Cold Chamber tests. (See text for explanation of letters.)

Appendix E, Exhibit 1APPENDIX EComparison of PRF Data with That from Other Sources

EXHIBIT 1. Data from Civil Aeronautics Authority, Experimental Station, Indianapolis, Indiana. The Technical Development Service of the Civil Aeronautics Authority, conducts a program for testing the effectiveness of various agents in combating aircraft cylinder fires. For this particular study, a bench assembly was set up that consisted of a single cylinder of a radial aircraft engine (complete with baffles and plugs) mounted in an air duct, and extinguishing nozzle and a source of fire. In operation, a mixture of air, fuel, and lubricating oil was passed through the air duct and around the cylinder, and was ignited by applying a torch to the exhaust duct of the system. The contours of the duct around the cylinder were such that the flame was maintained on the leeward side of the cylinder, and did not progress to the fuel mixing chamber. Twenty seconds preburn were allowed before application of the agent. The agent was applied as follows:

a. A predetermined weight of agent was fed to a pressure cylinder at atmospheric, or elevated pressure, depending on the vapor pressure of the agent.

b. The cylinder was then pressurized by nitrogen to a predetermined pressure (500 psi in most cases reported here).

c. A quick opening valve was actuated to allow the agent to be forced from the nozzle into the flame area, the nozzle being located to provide optimum mixing of the agent with the fuel air mixture involved.

The effectiveness of an agent was determined by varying the amount of agent placed in the pressure chamber in a series of trials, and noting whether or not a given amount of agent extinguished a fire. The maximum amount which repeatedly extinguished a fire was recorded as the measure of the efficiency of the agent. Check runs were made with methyl bromide each time a compound was investigated. The data from these tests are presented in Table XXII, together with the weight of agent required and a calculation of its efficiency in terms of methyl bromide. The determinations were made using 20 seconds preburn, a large double slot nozzle, and a pressure of 500 psi. The data are reproducible to 0.01 pound of the agent.

Table XXII. Results of CAA Bench Tests of Fire Extinguishing Agents

Agent	Halon No.	Amount Used (lb)	Weight effectiveness ^a (%)
Methyl bromide	1001	0.10	100
Chlorobromomethane	1011	0.13	77
Methyl iodide	10001	0.15	67
Carbon tetrachloride	104	0.24	42
Dachlaurin ^b	...	0.27	37
Carbon dioxide ^c	...	0.60	17
1,2-dibromotetrafluoro- ethane	2402	0.11	91
Tetrabromoethane	2004	0.21	48
Bromodichloromethane	1021	0.12	83
Tribromomethane	1003	0.08	125
Bromotrichloromethane	1031	0.13	77
Dibromochloromethane	1012	0.10	100
Ethyl bromide	2001	0.16	63
1,2-dibromoethane	2002	0.14	72
Dibromomethane	1002	0.11	91
1,2-dibromo 3-chloro- propane	3012A	0.23	43

(a) Methyl bromide = 100%.

(b) An agent incorporating carbon dioxide and chlorobromomethane.

(c) Application pressure 800 psi.

The CAA report noted that this table gives a comparison of agents under one arbitrary condition only, and pointed out that it is possible that some agents may be more effective when discharged through a different size or type of nozzle and/or at a different pressure. They reported that in preliminary investigations, at pressures from 100 psi to 600 psi, and using large, medium, and small nozzles of the same design, the results indicated that methyl bromide was most effective when used with the medium sized nozzle at 200 psi, requiring .09 pounds of agent to extinguish the fire.

The curve in Fig. 15 compares the weight efficiencies estimated from the PRF data with those calculated from the CAA data. It is seen that carbon dioxide does not produce a point near the apparent function, probably a result of difficulty in testing carbon dioxide in the bench test because of its high vapor pressure (approximately 800 psi). The smaller deviations from a linear relationship probably result from:

- (1) The application rate characteristics of individual

compounds in the bench test (see Table XXII).

(2) A difference between the flammable material concentration in the bench test and the flammable concentration in the flame inhibition test (i.e., the bench test may employ a concentration of flammable differing from that at peak flammability).

(3) The possible effect of molecular weight on such properties as rate of diffusion (this is not considered in the weight efficiency estimates based on PRF data).

(4) A pressure in the fire zone of the bench test differing from that in the flame inhibition tests.

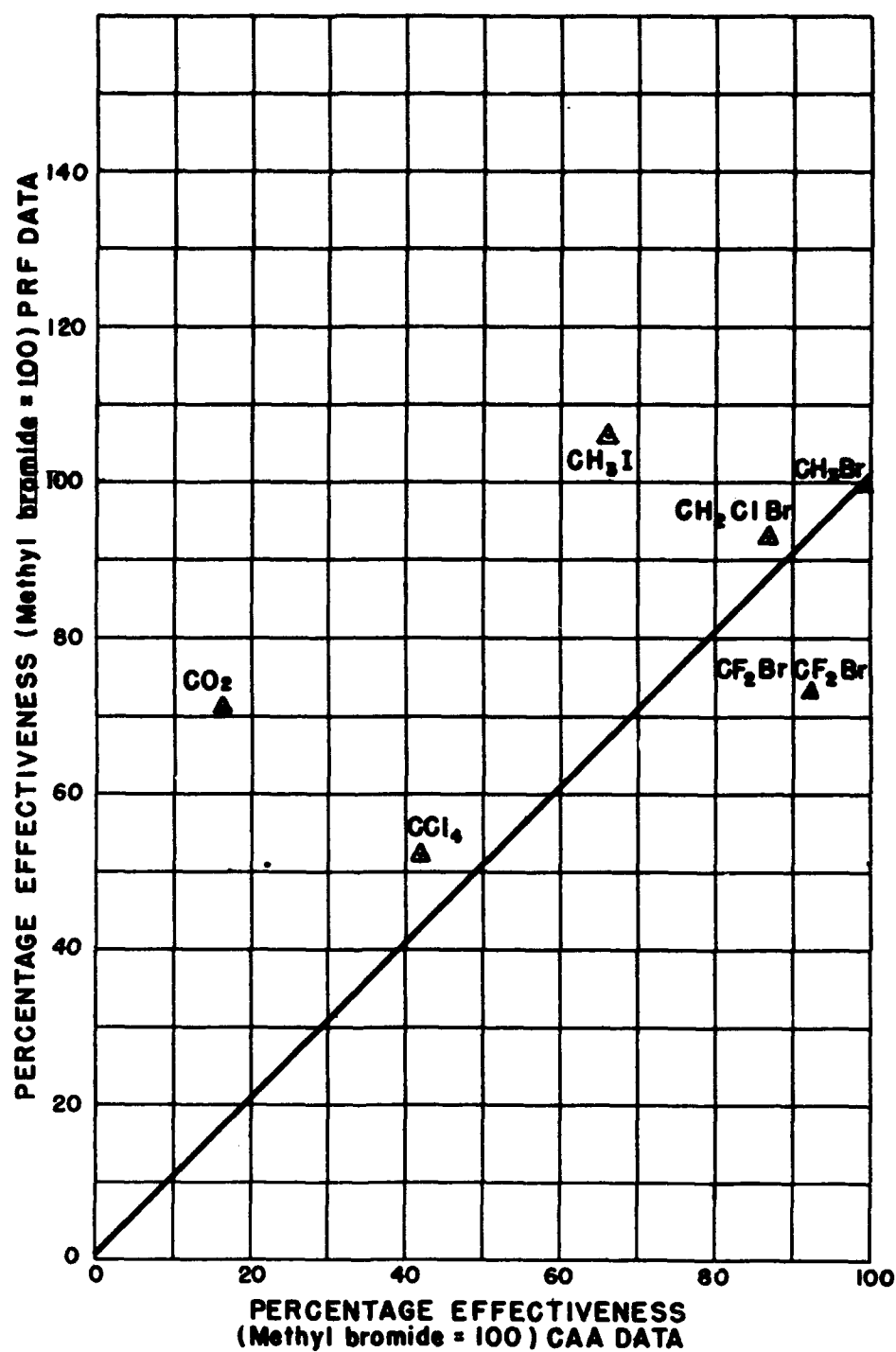


Fig. 15. Effectiveness of agents tested by the CAA compared with similar data from the PRF.

Appendix E, Exhibit 2

EXHIBIT 2. Comparison of PRF Data with Similar Data from Minnesota Mining and Manufacturing Company. The following description of the test method used is taken from a report of the New Products Division of the Minnesota Mining and Manufacturing Company, Fluorocarbons as Fire Extinguishing Agents, 5 November 1948. The reporting organization emphasized that the data obtained by this method are comparative and limited to this particular test, and were taken for the purpose of preliminary or "screening" investigation.

The report stated that the method used to compare the efficiencies of the fluorocarbons with other types of fire extinguishing agents was essentially as follows: A five-gallon can, lacquered on the inside, was equipped with a mixing fan, an observation window sealed and clamped to the top of the can, a large rubber stopper inserted in the hole at the top of the can, and a gas inlet tube at the bottom of the can. The desired amount of liquid or gas was introduced into the can, and the can was immediately closed. The fan was started and the gases were mixed for five minutes. The liquid samples were evaporated quickly by applying heat, and then the system was cooled to room temperature before beginning the test. After the five-minute period, the fan was stopped. Cotton (0.5 g) in a wire basket (copper or nichrome) was wet with 10 drops of heptane and ignited, and the flaming cotton was thrust into the can. After the flame was extinguished, the cotton was removed, and air was blown through the system for ten minutes before another test was begun.

The experimental results from the above report are summarized in Table XXIII, in which the comparative effectiveness has been calculated for the agents which were also evaluated at Purdue. Since a direct basis of comparison did not exist (methyl bromide was not tested by MM&M), carbon dioxide was used as the key compound, its percent effectiveness (71%) being assumed to be the same in this test as it was in the other. Comparison of these data with equivalent data from the PRF is shown in Fig. 16.

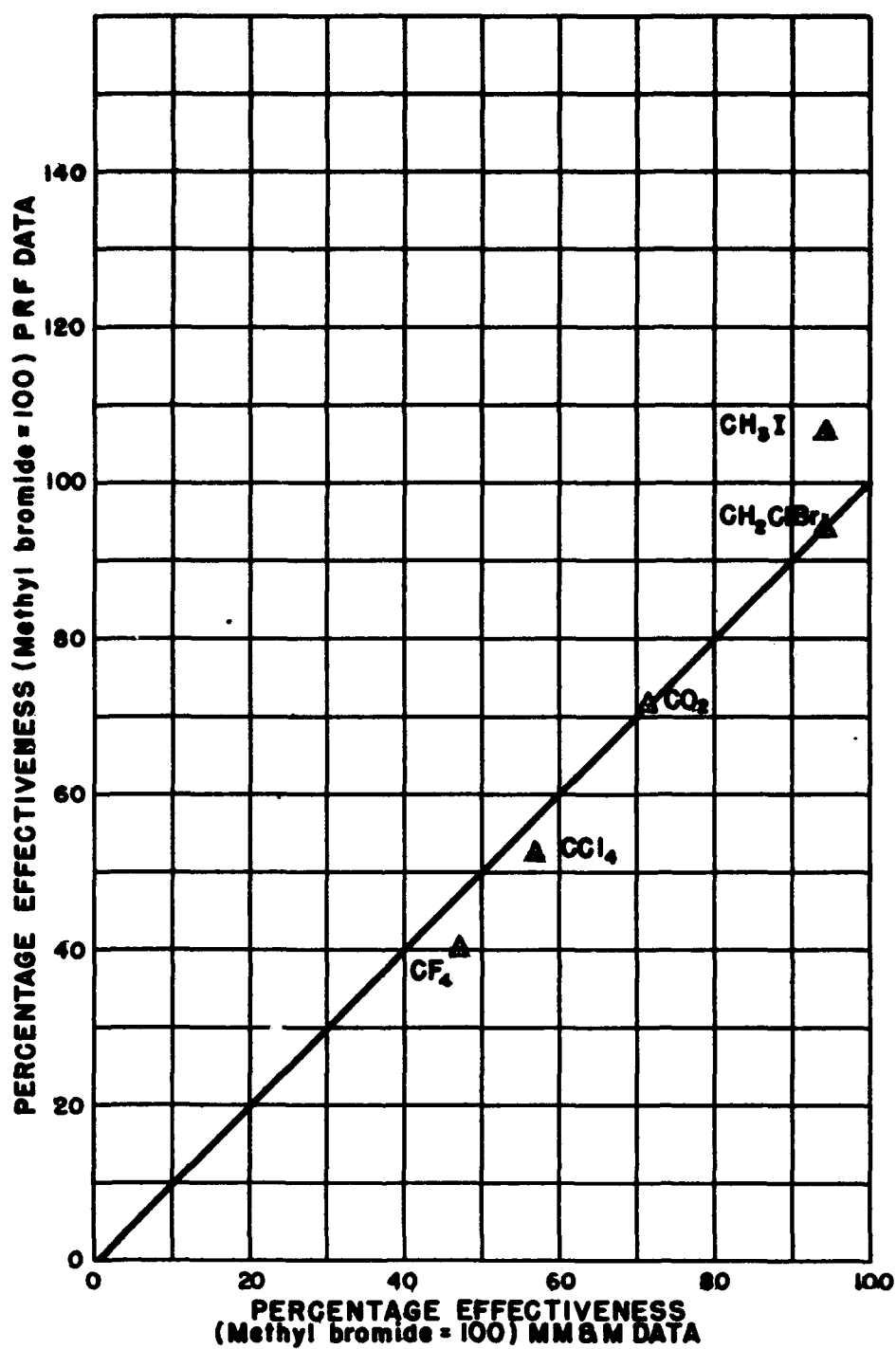


Fig. 16. Effectiveness of agents tested by the Minnesota Mining and Manufacturing Company compared with similar data from the PRF.

**Table XXIII. Summary of Results of Fire Tests
by Minnesota Mining and Manufacturing Company**

Agent	Halon No.	Boiling Point (Deg. C)	Approximate Amount to Extinguish Flame Instan- taneously (% by Wt. in Air)	Effective- ness (%) ^a
Carbon tetrafluoride	14	-129	28-33	47
Hexafluoroethane	26	- 78	28-31	
Octafluoropropane	38	- 38	29	
Octadecafluoro- dibutylether	-	99	35-40	
Chlorobromomethane	1011	69	15	95
Carbon tetrachloride	104	77	25	57
Carbon dioxide	-	-	20	71 ^b
Dichloromethane	102	40	25-30	
Methyl iodide	10001	42	15	95

(a) Methyl bromide = 100%

(b) See text in previous paragraph.

Appendix E, Exhibit 3

EXHIBIT 3. Data from English Sources. In an intelligence report, the Air Force Attache in London reported data developed by the Pyrene Co., Ltd. (London).¹ Burgoyne and Richardson, of the Imperial College of Science & Technology, London, have reported the results of similar tests.² Table XXIV shows the concentrations of agents (in grams per liter of air) found by the Pyrene Co. to be necessary to extinguish n-heptane fires at normal temperatures and pressures. It also shows the concentrations of agents in air, expressed as volume percent, found by Burgoyne and Richardson to be necessary to extinguish n-hexane liquid fires instantaneously. For each of these, the percent effectiveness was calculated in the manner previously reported in Appendix E, Exhibits 2 and 3.

Table XXIV. Results of Fire Tests by English Investigators

Agent	Halon No.	Pyrene Co., Ltd		Burgoyne & Richardson	
		Conc.	Effective- ness (% by Wt) ^a	Conc. (% by Vol)	Effective- ness (% by Wt) ^a
Methyl bromide	1001	0.09	100	5.5	100
Methyl iodide	10001	0.28	68	-	-
Carbon tetrachloride	104	0.33	58	7.2	47
Carbon dioxide	-	-		22	53.5

(a) Methyl bromide set at 100%

¹ Air Force Intelligence Report 817-48, "Aircraft Fire Protection," 3 May 1948, p. 3.

² J. H. Burgoyne and J. F. Richardson, "Extinguishing Burning Liquids", Fuel 28, 7 (1949) p. 155.

APPROVAL OF
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30 OCT 1950

IN REPLY
REFER TO: TECRD ASI.
8-76-04-003

SUBJECT: Transmittal of Report 1177, Interim Report, Vaporizing Fire Extinguishing Agents

THRU: Commanding General
The Engineer Center and Fort Belvoir
Fort Belvoir, Virginia

TO: Chief of Engineers
Department of the Army
Washington 25, D. C.
ATTENTION: Chief, Engineer Research and Development Division

1. Transmitted herewith is Report 1177, "Interim Report, Vaporizing Fire Extinguishing Agent," dated 18 August 1950, which was prepared by the Technical Staff of the Engineer Research and Development Laboratories. This interim report covers laboratory tests and research to develop a superior fire extinguishing agent, of low toxicity, suitable for use by troops in hand-portable containers under all climatic conditions.

2. The report concludes that:

a. Of all the agents tested, bromotrifluoromethane best suits the actual military requirements for a fire extinguishing agent, and is superior to methyl bromide and carbon tetrachloride.

b. As a military fire fighting agent, dibromodifluoromethane is equivalent to bromotrifluoromethane in all respects except that of toxicity.

3. The report recommends that service tests be conducted on bromotrifluoromethane as a fire extinguishing agent for Class B and C fires.

TECRD ASI
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Extinguishing Agents

4. The report with its conclusions and recommendations is approved.

- 2 Incls
1. Proposed distr list
(in quint)
2. Rpt 1177 (in quad)

O B Beasley
O. B. BEASLEY
Colonel, CE
Commanding

TECAG 3191

Ind Ind

Hq, The Engr Cen & Ft Belvoir, Ft Belvoir, Va. 30 OCT 1950

TO: C of Engrs, DA, Washington 25, D. C.

✓ 3 chuds
N/C

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SUBJECT: Transmittal of Report 1177, Interim Report, Vaporizing Fire Extinguishing Agents

ENGHC(30 Oct 50)

2nd Ind.

Office of the Chief of Engineers, Washington 25, D.C.

8 November 1950

TO: The Commanding General, The Engineer Center, Fort Belvoir, Virginia

1. The recommendation paragraph 22, page 43 of the subject Interim Report 1177, entitled Vaporizing Fire Extinguishing Agents is approved.

2. The proposed distribution list inclosed with the basic letter is approved except that the Office Technical Services, Department of Commerce shall be deleted from the list.

BY ORDER OF THE CHIEF OF ENGINEERS:

1 Incl

1. Proposed distr list
(4 cys w/d)
2. w/d

D. G. Hammond
D. G. HAMMOND
Lt. Colonel, Corps of Engineers
Chief, Engr. Res. & Dev. Div.
Military Operations

TECAG 319.1

3rd Ind

Hq. The Engr Cen & Ft Belvoir, Ft Belvoir, Va. 10 NOV 1950

TO: CO, E.R.D.L., Ft Belvoir, Va.

1 incl
4c